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SRI Project PAU-4900

## PYROTECHNIC DISSEMINATION RESEARCH STUDIES

Special Technical Report No. 16

by

J. E. Baldwin  
C. E. Wooldridge

JUNE 1967



DEPARTMENT OF THE ARMY  
EDGEWOOD ARSENAL  
Research Laboratories  
Physical Research Laboratory  
Edgewood Arsenal, Maryland 21010

Contract DA-18-035-AMC-122(A)

STANFORD RESEARCH INSTITUTE  
Menlo Park, California

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DEPARTMENT OF THE ARMY  
EDGEWOOD ARSENAL  
Research Laboratories  
Physical Research Laboratory  
Edgewood Arsenal, Maryland 21010

Contract DA-18-035-AMC-122(A)  
Task 1B522301A08101

STANFORD RESEARCH INSTITUTE  
Menlo Park, California

## FOREWORD

The work described in this report was authorized under Task 1B522301A08101, Contract DA-18-035-AMC-122(A), "Dissemination Investigations of Liquid and Solid Agents (U)." As outlined in the report only pyrotechnic dissemination is discussed in this publication. The other major method of thermal dissemination, which utilizes a rocket motor, is discussed in Special Technical Report No. 4. This work was started in April 1964 and completed in May 1967.

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## Acknowledgments

The chemical analyses of the CS and MAA formulations were performed by Norman A. Kirshen. The authors take this opportunity to express appreciation to Walter H. Johnson and Irvin A. Illing, Engineering Assistants, for their long hours of work under the necessarily uncomfortable conditions.

## DIGEST

This document reviews recent work accomplished toward the development of an understanding of the processes involved in pyrotechnic dissemination. An initial literature survey showed that many important phenomena had never been investigated in previous studies on pyrotechnics and model compounds, including the temperature profile through the combustion wave, the effects of operation at pressures other than ambient, and the effects of both chemical formulation and physical processing parameters on the output efficiency of pyrotechnics.

The experiments which were performed to investigate these areas included adiabatic self-heating (ASH) measurements, differential thermal analysis (DTA) measurements, burning rate measurements as a function of pressure, temperature profile measurements in the combustion zone, and agent yield measurements utilizing a total recovery technique. A concurrent effort was made to develop a useful computer program which could predict the effects of formulation changes.

The ASH experiments defined the activation energy of a typical pyrotechnic and of binary mixtures of its ingredients and showed that a burning-rate derived activation energy is necessarily unreliable because of its dependence on the physical process of heat transfer. The DTA measurements defined the endotherms and exotherms to be expected as a function of temperature and were demonstrated to be a useful tool for screening out experimental mixes which have an exotherm at a dangerously low temperature. Burning rate studies indicated that pyrotechnics have a burning rate law which resembles that of solid rockets. Temperature profile measurements indicated that there is a significant preheat zone ahead of the combustion wave and that the char bed remaining after passage of the wave can significantly influence agent decomposition. Agent yield measurements demonstrated that larger pyrotechnics were more effective than small ones and that the dissemination efficiency can be correlated with the agent residence time.

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## I INTRODUCTION AND BACKGROUND

The purpose of this document is to review the work accomplished under Contract DA 18-035-AMC-122(A) in the field of thermal and pyrotechnic aerosol production processes. The studies were instituted in April 1964 and terminated in May 1967. Goals of this work were to develop an understanding of the processes involved in pyrotechnic dissemination and to pursue in necessary depth those approaches offering the highest probability of extending the state of the art and providing maximum usefulness of these techniques.

At the start of the program a literature search was made to determine the problem areas which exist in the pyrotechnic field. Since the pyrotechnic dissemination of dyes and smoke additives parallels the dissemination of agents this work was also included in the survey.

The work reviewed showed that in the generation of smoke or agent aerosols by pyrotechnic means, nearly all methods utilized a potassium chlorate ( $\text{KClO}_3$ ) based pyrotechnic. Exceptions were exotic experimental mixes such as compositions containing "Pyrofuse" and novel experimental castable compositions. (The Pyrofuse reaction utilizes the heat of alloying of aluminum with palladium.) Many other oxidizers have been evaluated in the past but all have been abandoned, usually because of the excessive flame temperature produced. Some more recent work has investigated a wider range of oxidizers and fuels than those commonly considered. Many attempts were made by these investigators and others to use different organic and inorganic oxidizers, but none were completely successful. Potassium chlorate still appears to be the most useful oxidizer for all smoke or agent aerosol-producing pyrotechnics because of its ease of ignition, its smooth burning, and its ability to maintain combustion at low temperatures and pressures.

Sugar, lactose, and other similar materials which oxidize easily at low temperatures are normally used as fuels. Sulfur is used predominantly in smoke-producing compositions. Its main drawback is the

question of its shock sensitivity in combination with  $\text{KClO}_3$ ; several accidents have been reported which have been attributed to the sulfur- $\text{KClO}_3$  combination. Nitrocellulose (NC), often used as a binder, functions as a combination fuel-oxidizer. Carbonates, bicarbonates, kaolin, and other coolants are added to absorb heat and to provide a uniform flame temperature and a suitable atmosphere for evaporation of agent. These compounds tend to detract from the overall effectiveness of pyrotechnic systems and are particularly undesirable for castable systems since the fine particle size of the coolants makes casting difficult.

The incorporation of burning rate catalysts has not been particularly rewarding in the pyrotechnic field. Incorporation of a palladium catalyst<sup>1</sup> allowed 64 percent of methylaminoanthraquinone (MAA) to be disseminated without degradation when  $\text{KClO}_3$  was used as an oxidizer and the temperatures were reported to be very low. The cost of the palladium catalyst limits the use of such a system to the laboratory since relatively large quantities must be used to maintain combustion. Unreported confirmatory tests at Edgewood Arsenal showed considerable amounts of dye were not disseminated and the experimental munition tended to flame and exhibited other undesirable characteristics.

It appears that, in general, future gains in pyrotechnic performance will depend on the formulation of castable compositions which can be more uniformly processed and which will allow improved loading densities of disseminant. (The work of Resin Research Laboratories in the development of thio-syrups for use as pyrotechnic binders appears promising ) Additional work to develop low cost burning rate catalysts would also be useful. Increased burning rates obtained without the penalty of an increased flame temperature would decrease the residence time of agent in the hot combustion zone and thus decrease its degradation. Finally, the most efficient use of existing pyrotechnics requires a better definition of weapon design parameters in order to optimize both delivery and area coverage.

The other major dissemination technique which has been historically investigated is termed hot gas dissemination. In this method the disseminant is not mixed in the fuel-oxidizer matrix as it is in a pyrotechnic, but instead it is vaporized by the hot combustion products downstream of the flame zone.<sup>4-6</sup> Gas generators commonly employed

in the past for both laboratory and development studies have utilized propane and air, sodium chlorate and gilsonite, and ammonium nitrate and rubber<sup>5,7</sup> as combustible combinations. The agent or simulant to be dispersed was injected into a low velocity region where the material was converted to an aerosol principally by thermal energy. The process of thermal vaporization with subsequent condensation produces aerosols with volume-to-surface mean particle diameters ( $D_0$ ) usually smaller than 10 microns.

The propane and air furnace has been used extensively for the generation of a hot gas under controlled conditions. This allows the parametric study of the effects of important variables such as environmental temperature and gas velocity on both the yield and the particle size distribution obtained from hot gas atomization. An important result is that aerodynamic forces contribute significantly to particle breakup when the gas velocity is sufficiently high so that both thermal and kinetic energy must be considered. Significant progress has been made in defining many of the important variables.<sup>4-7</sup> However, it was found that the description of particle size distributions in the generated aerosol required a separate equation for each injectant under each set of experimental conditions. A true understanding of the processes involved, which could result in a universal correlation of the data, still eludes the investigators. Interestingly enough, many studies which have been made on similar problems concerned with propellant vaporization<sup>8,9</sup> and the breakup of liquid jets in high velocity gas streams<sup>10,11</sup> do not appear to have been properly exploited by workers in this field.

The principal variable which must be controlled in any dissemination technique is the environmental temperature to which the disseminant is exposed because high temperatures will produce excessive degradation. The principal advantage of hot gas dissemination is that it offers the possibility of a nearly inexhaustible range of gas compositions from the entire spectrum of solid propellants which have been developed for propulsion purposes. In addition, any desired temperature is available

in the exit cone of a nozzle where the temperature is a strong function of area ratio. However, a complicating factor is that the nature of the carrier gas can influence the decomposition rate of the agent being dispensed. Additionally, solid particles of metallic chloride in the exhaust gas formed by the combustion of potassium chlorate or sodium chlorate are suspected of providing nucleation surfaces for condensing liquids, thereby affecting the particle size distribution. Obviously, the utilization of hot gas atomization has many frontiers to be explored; Stanford Research Institute work in this promising area is reviewed below.

In general, the hot gas dissemination technique provides a method for ejecting either liquids or fluidized solids with a minimum of degradation. Two modes of particle size are possible--one of which lies below 10 microns and is produced by evaporation and subsequent recondensation, and one of which lies above 10 microns and is produced by aerodynamic breakup of larger injected particles. A controlled atmosphere during dissemination is possible with selection of mass flow, composition, and temperature being available. In addition, the flashing (rapid combustion) of sensitive agents may be eliminated by flow control of components. Further work should be done in this area to explore possible applications of secondary injection devices.

As reported above, work done by other investigators has primarily been concerned with injection of the agent or simulant into a high temperature, relatively low kinetic energy gas stream at Mach 1 or less. In contrast, studies here at the Institute have considered injection of the disseminant into a gas stream which has been expanded to velocities on the order of five times the speed of sound. Since the gases are cooled upon expansion, the environmental temperature to which the agent is exposed can be controlled, and in addition the aerosol can be discharged with significant kinetic energy toward a chosen target.

The technique developed at Stanford Research Institute utilizes a rocket motor with an integral tank which is pressurized by the chamber

gases. The tank is filled with the fluid material to be aerosolized. Fluid is forced from the chamber into the gas stream which has been expanded through a De Laval nozzle. Nominal conditions which have been studied are 1000 psia in the fluid chamber and 25 psia at the injection point in the gas stream where the gas stream has a velocity corresponding to approximately Mach 5 with a temperature of approximately 1200°F. The injected fluid stream is directed at right angles into the gas stream resulting in a complex system of shocks accompanied by a very turbulent mixing region both in the nozzle and in the area immediately behind the nozzle. Mixing in the plume is enhanced by the ingestion of large amounts of air into the generated plume.

The experimental studies performed using the rocket motor dissemination technique have been reported in Special Technical Report No. 4 entitled, Secondary Injection of CS Agents into a Supersonic Rocket Exhaust. This work was concluded with the firing of three test units containing agent CS. A summary of the data from these tests is presented in Table I.



TABLE I

RESULTS OF HOT GAS DISSEMINATION OF CS-TESTS 1, 2, AND 3

	Test 1	Test 2	Test 3
Motor Data			
Propellant type	PU 128*	PU 128*	PU 128*
Expansion cone angle (deg.)	15	15	15
Throat outside annular diameter (in.)	1.525	1.525	1.525
Throat inside diameter (in.)	1.250	1.250	1.250
Exit diameter of nozzle (in.)	2.940	2.940	2.940
Propellant weight (g)	2458	2453	2372
Igniter type	Mg-Teflon	Mg-Teflon	Mg-Teflon
Safety pressure (psi)	3000	3000	3000
Design Injector Data			
Injector hole diameter (in.)	0.050	0.0325	0.050
Number of holes	54	126	100
Fluid temperature (°F)	58	---	---
Agent type	CS- $\text{H}_2\text{O}$	CS-DMEF	CS- $\text{CH}_2\text{Cl}_2$
Performance Data			
Burn time (sec)	1.18	1.16	1.27
Injector time (sec)	0.87	1.17	1.26
Particle size 50% by weight (microns)	3	2	1.5
Percent CS recovery based on computed discharged IOL/CS ratio <sup>a</sup>	82	92	59
Agent Loading Data			
Weight of CS charged (g)	2640	3320	5400
Weight of fluid charged (g)	4400	4600	19200
Weight of CS disseminated (g)	2640	3320	1705
General			
Device dimensions (in.)	6 x 30	6 x 32	6 x 54

<sup>a</sup>PU 128 - 78%  $\text{HClO}_4$ , 2% Thermax, 20% polyurethane binder.  
<sup>b</sup>The measured purity of the CS used was approximately 92%.

## II METHOD OF APPROACH FOR CURRENT STUDIES

The current effort has been directed toward an understanding of the behavior of heterogeneous pressed systems which are in common use (the exact formulations studied were selected from those recommended by Edgewood Arsenal). If a satisfactory castable composition were available, many of the existing pyrotechnic problems would be eliminated. However, our investigation was limited to pressed compositions.

The literature survey discussed above indicated that much of the basic data needed for orderly weapon design and formulation development were missing from studies performed earlier on existing pyrotechnics and model compounds. The most important unexplored points were:

1. The true yield of existing pyrotechnics; i.e., the percentage of agent which survives the combustion process. Values have been obtained which vary from very low yields to yields in excess of 100 percent.
2. The true flame temperature of the pyrotechnic and the temperature profile in the combustion wave.
3. Information on the true operating pressure of pyrotechnics and the effects of operation at pressures other than ambient. The effects of pressure on burning rate and residence time appeared to need assessment.
4. Definition of the effects of physical processing parameters on the efficiency and burning rates of pyrotechnic mixes. The relationship of formulation to yield, by-product formation, and functional reliability was in need of clarification.
5. The role of coolants in the different formulations. This has never been adequately explained.

In order to gain additional insight into pyrotechnic processes and to derive the design parameters governing the effective generation of an aerosol, it is necessary to obtain a better description of the thermal and chemical processes which occur during combustion. It was recognized that a broad spectrum of experiments was needed to advance our understanding. In particular, a careful mass balance of the pyrotechnic process was needed to clarify the role of the various ingredients and decomposition products of the aerosol and residue. The following experimental program was outlined to provide the necessary information. Our program was directed toward basic measurements which had not been made previously.

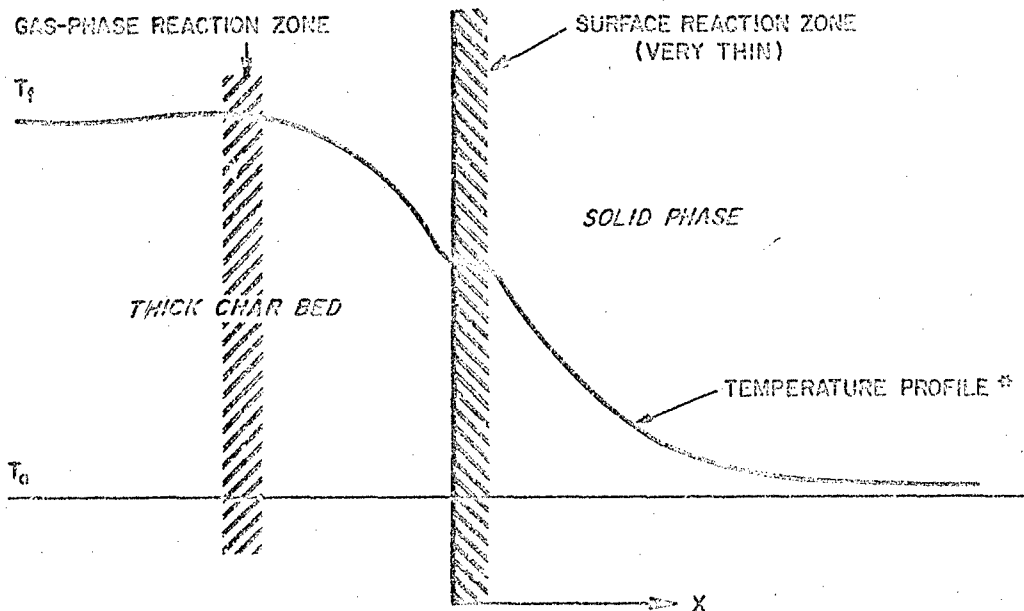
Adiabatic self-heating (ASH) measurements were made to provide values of the activation energy. Differential thermal analysis (DTA) measurements were made on various pyrotechnic components to provide data on melting points, phase changes, and reaction temperatures. A technique for obtaining burning rate measurements under pressure was developed for pyrotechnics, and burning rates were evaluated for two common formulations as a function of pressure. Thermal conductivity measurements were made for common ingredients incorporated into pyrotechnics. Vapor pressure as a function of temperature was determined for methylenecanthraquinone (MAA), a red dye often used as a simulant for agent (S).

Temperature profile studies of the combustion zone were designed to yield information on the thickness and temperature distribution of the zone. Agent yield measurements were made utilizing a total recovery technique. The temperature profile and agent yield measurements using thermocouple and photographic techniques were made in pyrotechnic hardware to duplicate actual conditions.

Lastly, an effort was made to develop useful computer techniques utilizing the information obtained on the physical and chemical properties of pyrotechnic ingredients. Portions of the experimental results were included in the program input information to limit certain parameters of the computation and to prevent complete chemical equilibrium from being simulated by the computer.

### III LABORATORY EXPERIMENTS

In order to develop an understanding of the factors involved in the combustion of pyrotechnic and propellant composition, it is appropriate to examine the model depicted in Fig. 1 which represents the key processes.



\* EXOTHERMIC CONDENSED-PHASE REACTIONS AND ENDOTHERMIC AGENT, BINDER, OR OXIDIZER PYROLYSIS AND PHASE CHANGES OCCUR IN THE PREHEAT ZONE UNDER THE TEMPERATURE PROFILE

TA-4500-710

FIG. 1 PROFILE OF COMBUSTION ZONE

In steady-state combustion an invariant temperature profile is established across the combustion zone; the limits of this profile are the initial ambient temperature of the pyrotechnic powder ( $T_0$ ) at the lower boundary and the local flame temperature at the upper boundary ( $T_f$ ). Heat energy is transferred from the flame to the condensed phase at a rate governed primarily by the temperature gradient between the flame and the surface of the condensed phase. Although the heat transfer

in the condensed phase is controlled in a similar manner, the exact temperature profile shape is modified by the thermal diffusivity of the medium concerned and is, of course, affected by the location of exothermic and endothermic reactions occurring in the gaseous and condensed phases. It is thus apparent that the actual physico-chemical model is rather complex; however, certain well-defined deductions can be made about the dependence of the burning rate on the initial powder temperature and the nature of bulk reactions that may occur at elevated temperatures (thermal explosion or autoignition reactions).

In composite propellant combustion it is recognized that the temperature dependence of the burning rate is related to the change in flame temperature which is caused by the ambient enthalpy variation, to the associated change in the surface temperature, and to the concomitant effect on the overall reaction rate, which was assumed to obey an Arrhenius-type expression ( $k = Ae^{-E_a/RT}$ ). In this regard it should be noted that the combustion of pyrotechnic mixes is very complex compared with the simple reactions ordinarily described by the Arrhenius equation. The values obtained are therefore not equivalent to those ordinarily derived in kinetic studies; however, limited analogies can be made. It is quite obvious that the appropriate temperature to use in an Arrhenius-type relationship is somewhat arbitrary, since the kinetically controlling reaction must occur in a zone where the temperature is somewhere between the flame temperature and the initial powder temperature. Attempts to identify the critical temperature can be made using differential thermal analysis (DTA) and adiabatic self-heating (ASH) techniques. These experiments suggest that for a sulfur- $KClO_3$  mix exothermic deflagration occurs at about  $117^\circ C$  (see table II, page 23); this could fix a lower bound for a critical surface or subsurface reaction temperature. The very low reaction temperature is due to the low heating rate.

The recent data on pyrotechnic burning rates at a range of elevated temperatures obtained by Edgewood Arsenal, and the burning rate-pressure relationship found as part of the present study, show that composite pyrotechnics burn in a similar manner to composite rock propellants. These data suggest therefore that the "pseudo activation energy" obtained from

the temperature sensitivity of the burning rate, as measured by Edgewood Arsenal is related primarily to the dependence of heat transfer on the temperature gradient between the gas phase and a critical reaction zone (perhaps at a solid surface or in a melted zone). The low value for the burning-rate-derived "activation energy" appears to be adequately explained by the temperature dependence of a physical process--that of heat transfer. It could, perhaps, be explained by a heterogeneous catalysis process: however, the analogous behavior of most double-base powders, composite powders, and pyrotechnics suggests that a physical rather than a chemical explanation is correct. Thus, one cannot directly compare the pseudo activation energy obtained from burning rate measurements with the value obtained from the ASH measurements discussed below.

#### A. Adiabatic Self-Heating (ASH) Experiments

The ASH technique is extremely useful for obtaining the overall activation energy of a complex combustion process. The present work was based upon an approach similar to that described by Gross and Amster.<sup>12</sup> The pressed pyrotechnic sample to be examined is set in the well of a small aluminum cylinder which is wrapped with a Nichrome heater. The sample is then heated to the temperature at which self-heating begins. The rising temperature of the sample is followed precisely by the temperature of the highly conductive aluminum block. The adiabatic control is accomplished by the apparatus shown in Fig. 2. Thermocouples located in the sample center and at the wall of the well measure any temperature difference between sample and environment. The differential voltage from the thermocouple pair is fed into a temperature control system consisting of the following: (1) Leeds and Northrup DC Null Detector, (2) Leeds and Northrup Series 60 current-adjusting-type control, and (3) magnetic amplifier. The magnetic amplifier delivers power to the control heater to maintain adiabatic conditions as the sample temperature rises. For each sample a plot of the logarithm of the rate of temperature rise (deg/min) versus the inverse temperature ( $^{\circ}\text{K}^{-1}$ ) is prepared. The activation energy of the sample is found from the slope of this plot,  $m = -E_a/R$ . The frequency factor,  $A$ , is the intercept of the curve with the  $1/T$  axis.

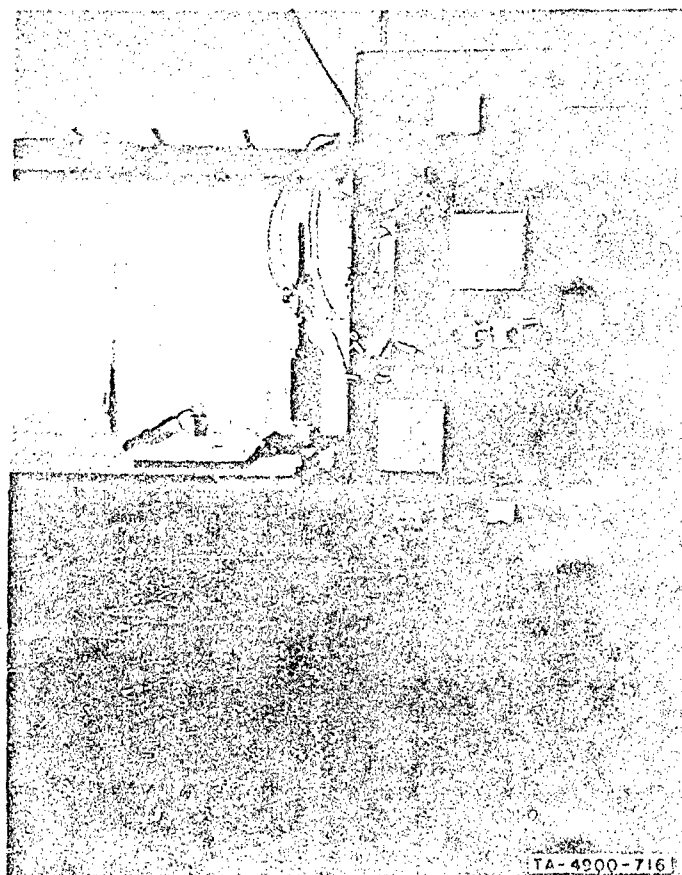


FIG. 2 ADIABATIC SELF HEATING APPARATUS

Table II presents data obtained by using the ASH technique on typical pyrotechnics and binary mixtures of component ingredients. It can be seen that very high values for the activation energy  $E_a$  are obtained for the complex pyrotechnic mixture, while the binary mixtures of sulfur and MAA with  $KClO_3$  give smaller values for  $E_a$ . It should also be noted that the binary mixtures deflagrated at different temperatures.

The data in Table II show that while the activation energy for both the redox mixtures of sulfur and MAA with oxidizer are the same, the comparative reaction rates (as measured by the frequency factor,  $A$ ) differ by several orders of magnitude. These data are highly significant, since they give us a method of comparing the relative oxidative stability of the agent and fuel components in the burning pyrotechnic mix. A way

is that open for comparing, and hence predicting, one aspect of the stability of agents and the reactivity of fuels in pyrotechnic mixes.

Table II

ADIABATIC SELF-HEATING DATA

Composition (wt %)	Onset Temperature (°C)	Ignition Temperature (°C)	Activation Energy, $E_A$ (kcal/g)	Frequency Factor, A
(1) 49.6 MMA 26.1 $KClO_3$ 10.3 Sugar 7.9 $K_2CO_3$ 5.1 KC	142 139	154.2 153.2	86 74.5	$1.7 \times 10^{14}$ $9.87 \times 10^{33}$
(2) 42 MMA (dextrinized) 23 $KClO_3$ 11 Sulphur 10 $K_2HCO_3$	not detected	183 183 183	not calculable	
(3) 10 $KClO_3$ 40 Sugar	128	133	not calculable	
(4) 40 $KClO_3$ 10 KC	154	160	64	$2.3 \times 10^{32}$
(5) 42 $KClO_3$ 28 Sulphur	80	117	45	$1.1 \times 10^{55}$
(6) 40 $KClO_3$ 60 MMA (dextrinized)		not measurable severe exotherm		
(7) 40 $KClO_3$ 10 MMA (dextrinized)	185	246	43.9	$1.1 \times 10^{30}$

Reaction rate adjusted to that present in a regular pyrotechnic mix.

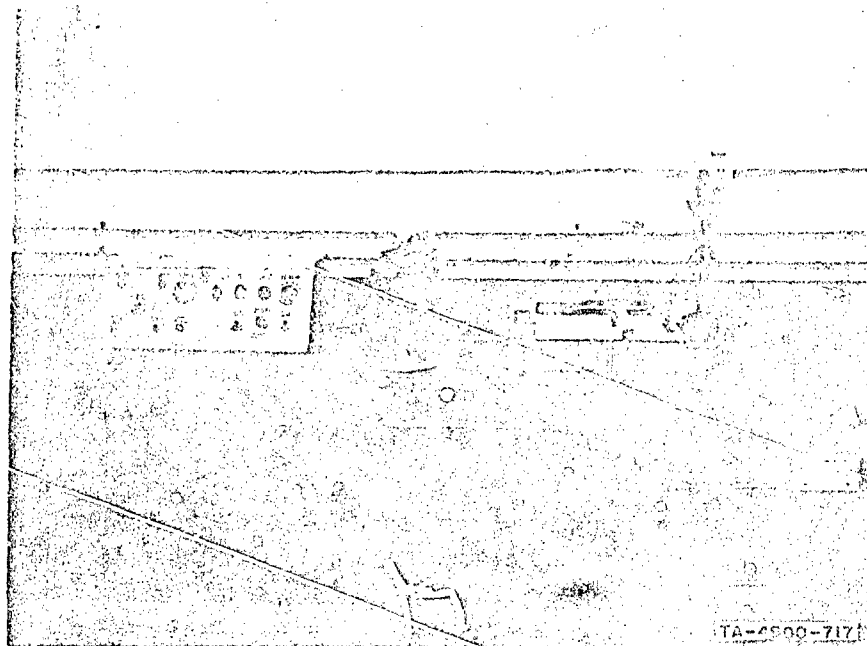


## E. Differential Thermal Analysis (DTA) Experiments

Another useful tool for studying the decomposition mechanisms involved in pyrotechnics is the DTA apparatus. The DTA technique accurately shows the endotherms and exotherms which appear as a compound or mixture of compounds is heated, reflecting both chemical reactions and physical effects such as melting points, phase changes, and crystal shifts. The apparatus employs two accurately matched thermocouples which are electrically wired to provide the differential emf as the output. This signal is then amplified and recorded as a function of sample temperature. One thermocouple is placed in each of two sample holders, one of which contains 5 mg of the material to be evaluated and the other of which contains 5 mg of aluminum oxide ( $\text{Al}_2\text{O}_3$ ). Both sample holders are placed in an electrically heated metal block. The temperature of the block is then raised at a uniform rate of  $10^\circ\text{C}/\text{min}$  while the differential temperature of the samples is recorded. Initially some problem was experienced due to convective air currents cooling the heating block. To alleviate this problem the entire block was covered by a small bell jar (Fig. 3(a)). A picture of the complete DTA apparatus including rate controller and X-Y plotter is shown in Fig. 3(b).

A series of DTA experiments have been performed with common ingredients used in pyrotechnics. The DTA trace for  $\text{KClO}_3$  (Fig. 4) indicates a melting point of  $365^\circ\text{C}$  in agreement with the literature<sup>13</sup> which reports values from 350 to  $380^\circ\text{C}$ . The exotherm is thought to be due to the decomposition of  $\text{KClO}_4$  which is reported to occur between 470 and  $580^\circ\text{C}$  depending on the purity of the sample. The reference<sup>13</sup> indicates that the decomposition of  $\text{KClO}_4$  should be endothermic. The exothermic reaction is reported to be due to crystallization of the by-products of decomposition. The second exotherm is postulated to be the result of crystal breakdown and resultant acceleration of oxygen generation.

The second trace (Fig. 5) is presented to show the effects of organometallic compounds on the decomposition of  $\text{KClO}_3$ . These compounds were tested as burning rate catalysts with little success, although  $\text{KClO}_3$  decomposition is clearly stimulated by addition of these compounds. Increased burning rates along with increased sensitivity would be expected from catalysis of the  $\text{KClO}_3$  decomposition. Burning rates were definitely increased through the addition of organometallic compounds but not to the extent desired. The use of the DTA to screen possible burning rate



(a) COMPLETE DTA ASSEMBLY



(b) DTA TEST CELL

FIG. 3 DTA APPARATUS

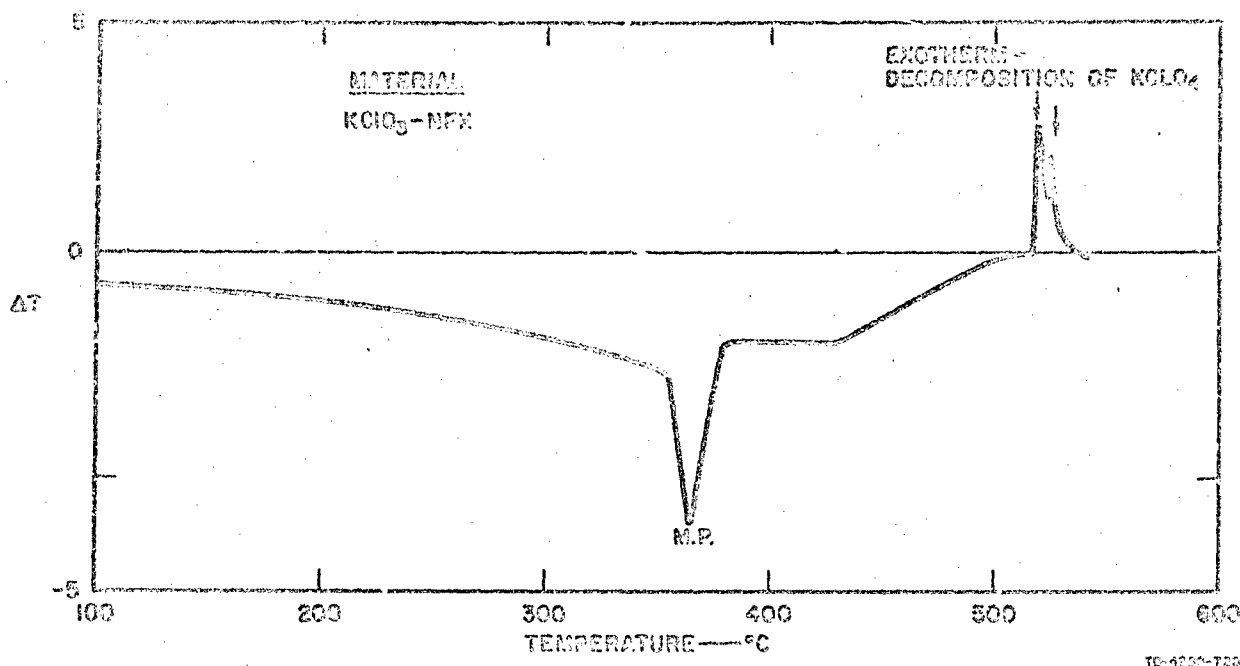


FIG. 4 DTA TRACE FOR KClO<sub>3</sub>

modifiers has been demonstrated on solid rocket propellant systems with success, and any serious burning rate studies for pyrotechnics should include DTA screening of possible catalysts.

Figure 6 is a DTA of the CS pyrotechnic mixture containing 40.6% CS, 25.2% KClO<sub>3</sub>, 3.2% NC, 11.6% kaolin, 19.4% lactose. The melting point of the CS is indicated by the first endotherm. Autoignition of the sample is indicated at approximately 210°C with self-heating starting at approximately 190°C. Each of the major ingredients were run individually and in combination. Lactose, Fig. A-1 (see Appendix), is seen to have an endotherm at 150°C and another at 220°C which is reported to be the melting point. The melting is apparently followed closely by exothermic decomposition at 230°C.

The CS DTA (Fig. A-2) indicates an endotherm at approximately 95°C (melting point 98°C) and another endotherm at 312°C (boiling point 311°C). A DTA of kaolin alone did not show any activity up to 600°C, the limit of our apparatus, although a decomposition endotherm was expected between 500 and 600°C.

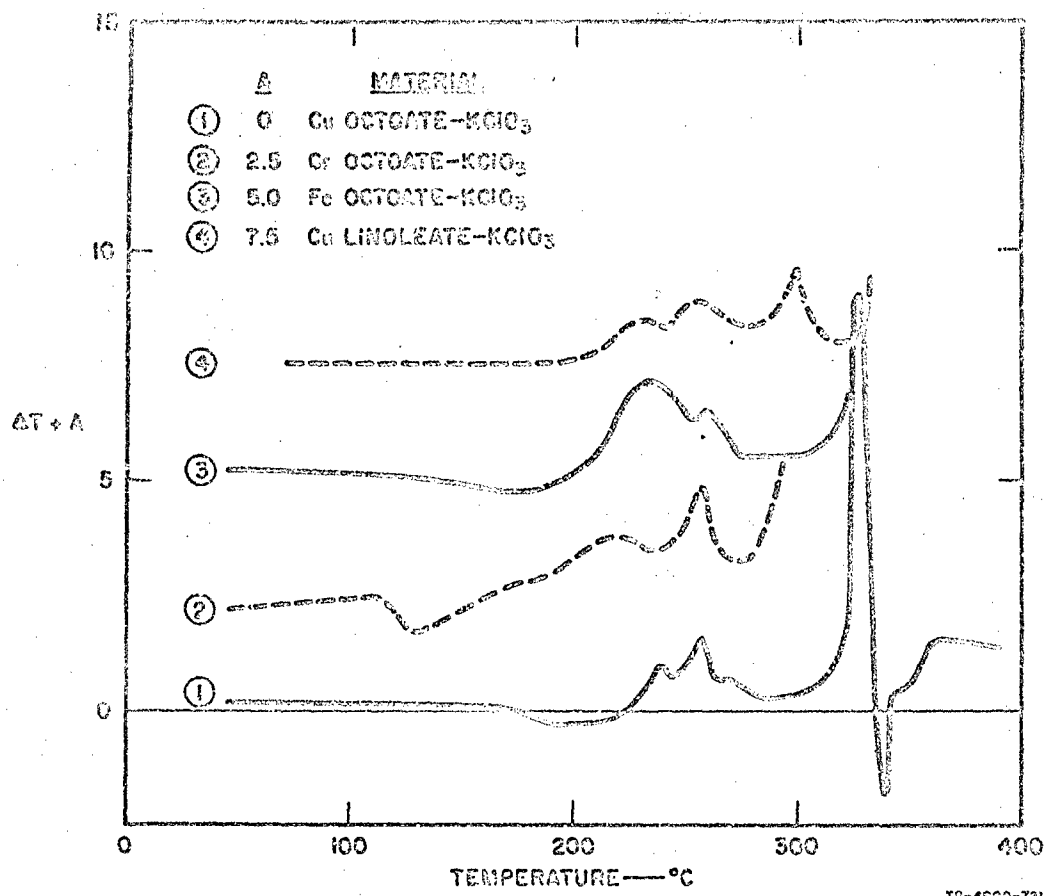


FIG. 5 DTA TRACES SHOWING EFFECTS OF ORGANO METALLIC ADDITIVES ON DECOMPOSITION OF KClO<sub>3</sub>

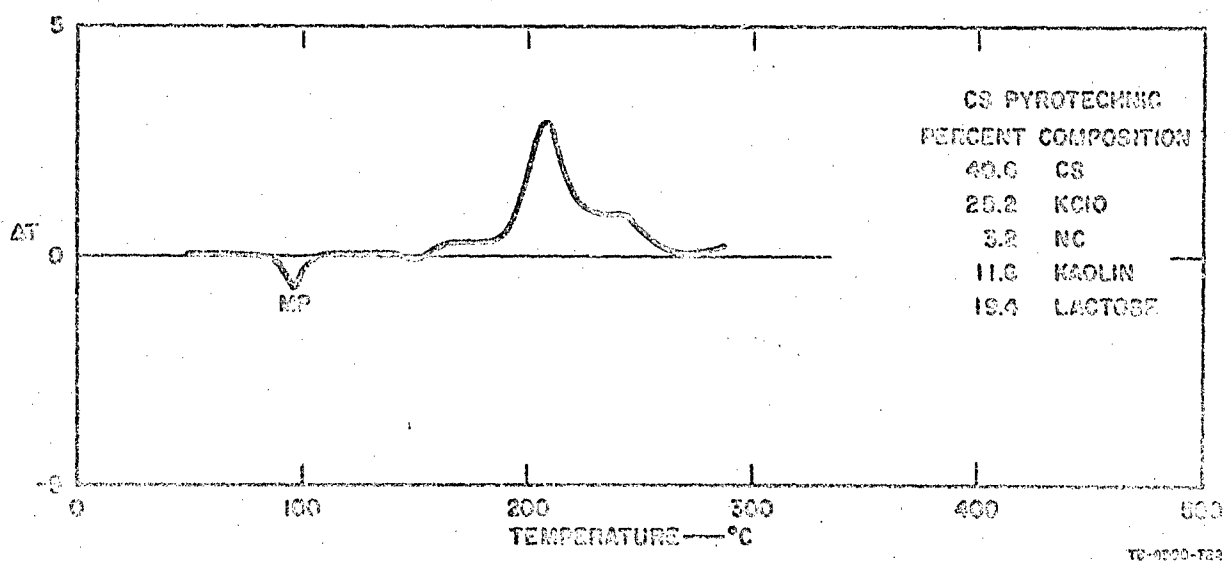


FIG. 6 DTA OF CS PYROTECHNIC MIX

Tests, mixtures of the ingredients were made so that possible interactions of ingredients might be detected. Figures A-3, A-4, and A-5 show the results from  $\text{KClO}_3$ -NC,  $\text{KClO}_3$ -lactose, and  $\text{KClO}_3$ -NC-lactose mixtures. These data indicate a very rapid exotherm at  $190^\circ\text{C}$  or less. Lactose with  $\text{KClO}_3$  resulted in a deflagration at approximately  $185^\circ\text{C}$  in both tests, while NC with  $\text{KClO}_3$  did not ignite and an endotherm is noted at  $330^\circ\text{C}$ . A mixture of CS and NC (Fig. A-6) shows no interaction, since the endotherms of CS and the exotherm of NC are evident.  $\text{KClO}_3$  and CS are shown to react (Fig. A-7) below  $275^\circ\text{C}$  and the typical CS endotherm at  $315^\circ\text{C}$  is not evident indicating destruction of the CS. A mixture of  $\text{KClO}_3$ -CS and lactose (Fig. A-8) shows the CS melting point and the lactose endotherm. The high exotherm at  $210^\circ\text{C}$  and the lack of an endotherm at  $315^\circ\text{C}$  indicates probable destruction of CS at well below  $300^\circ\text{C}$ .

A sulfur-CS mixture DTA (Fig. A-9) indicated no reaction between sulfur and CS up to the boiling point of the CS. This result is interesting, since all attempts to formulate a  $\text{KClO}_3$ -sulfur-CS pyrotechnic have failed. The DTA indicates that the reaction between sulfur and CS is not highly exothermic if a reaction does occur. Mr. Diener, Edgewood Arsenal, has indicated that a reaction between CS and sulfur does occur though the exact nature of the reaction is not known.

The DTA data from the MAA pyrotechnic ingredient combinations are shown in Figs. A-10 through A-19. This particular formulation is known to be somewhat shock sensitive and thermally unstable. Figure A-10 indicates a deflagration exotherm at under  $220^\circ\text{C}$ . A DTA of sulfur- $\text{KClO}_3$ , Fig. A-15, indicates an exotherm at  $175^\circ\text{C}$ . Addition of  $\text{NaHCO}_3$  to the mixture appears to sensitize it even more, and the rapid exotherm is shown to occur at  $165^\circ\text{C}$  (Fig. A-16). The  $\text{NaHCO}_3$  decomposition seen in Figs. A-13, A-17, and A-19 is completely absent in Fig. A-16. It is evident that there is an interaction between the three ingredients ( $\text{NaHCO}_3$ , S, and  $\text{KClO}_3$ ) which does not occur when only two of the ingredients are present. The overall decomposition is thought to proceed in the following manner:

$$\Delta H = -134.48 \text{ kcal/mole}$$



This reaction is probably activated by the generation of small amounts of water and carbon dioxide from the decomposition of  $\text{NaHCO}_3$  which lowers the initiation temperature of the  $\text{KClO}_3$ -S reaction.

The DTA is a versatile tool and provides significant information for a minimum of effort. Mixes which are experimental in nature may be screened using this technique, and those which show an exotherm at a dangerously low temperature may be discarded before further effort is expended in their development. For example, in a separate, unrelated experiment tellurium dioxide was being evaluated as a catalyst in a burning rate study. A sample was stored overnight in a relatively low temperature oven ( $120^\circ\text{F}$ ) and during the night the sample deflagrated. Another sample was then prepared and analyzed on the DTA apparatus; it was found that an exotherm existed at very low temperature ( $74^\circ\text{C}$ ) so that in retrospect, the deflagration was not surprising. If the DTA had been run before further work was attempted, this accidental ignition could have been avoided. The DTA was subsequently performed on all experimental formulations as a routine safety precaution. DTA results do not prove that a mix is safe to process, but they definitely indicate those which are unsafe because of a low temperature thermal instability. It should be noted that friction or impact sensitivity are not detected from DTA analyses.

The DTA apparatus is recommended as a standard test device for any group involved in pyrotechnic formulation work. Testing is simple, rapid, and low in cost. A high temperature DTA operable to  $1000^\circ\text{C}$  would be useful for determining the endotherms of various coolant materials which may be under evaluation.

#### C. Burning Rate Measurements

Very little information was found in the literature concerning the burning of pyrotechnics at pressures above atmospheric pressure. No burning rate curves were found for pyrotechnics as a function of pressure. Burning rates which were reported did not specify the pressure, indicating little concern on the part of researchers or designers with higher pressure operations.

At least two problem areas exist which could be potentially alleviated by higher pressure operation of pyrotechnics. The first of these is the burning rate problem. At the present time, no suitable low-cost catalysts are available for obtaining high burning rates, in the range 0.1 to 1.0 in./sec, at atmospheric pressure. The existing method for decreasing the burning time is to simply increase the burning surface area. However, burning rates of solid propellants and pyrotechnics are normally directly related to the pressure by a simple power function. Often a slight increase in pressure will increase the burning rate severalfold. In addition, a higher pressure provides for more efficient combustion of oxidizer and fuel combinations. This greater burning efficiency could result in a decrease in the fuel and oxidizer requirements for pyrotechnic formulations allowing greater concentrations of agent to be used. Higher pressure operation would also allow the design of larger devices which might move about under their own power as is currently done with existing "skittering" devices.

Pressure-burning rate data have been obtained for pyrotechnics containing MAA and CS over a range of pressures from 14.7 to 750 psia. These data were obtained in a Crawford strand bomb which was pressurized with dry nitrogen (Fig. 7). Constant pressure is maintained by bleeding off gas during burning, and burning is timed automatically by melting small wires which start and stop timers.

Pyrotechnic samples for burning rate determinations were pressed into cellulose acetate tubes using the die arrangement shown in Fig. 8. A series of five separate pressings were used on each sample to obtain a uniform strand density. Samples were 5/8 in. diameter by 2-1/2 in. long with metallic lead wires through them for clock starting and stopping. CS samples were fitted with a thermocouple in addition to the lead wires used for timing. The thermocouple was located inside the sample approximately 1/2 in. from the bottom. Figure 9 shows the method of holding the strand during burning.

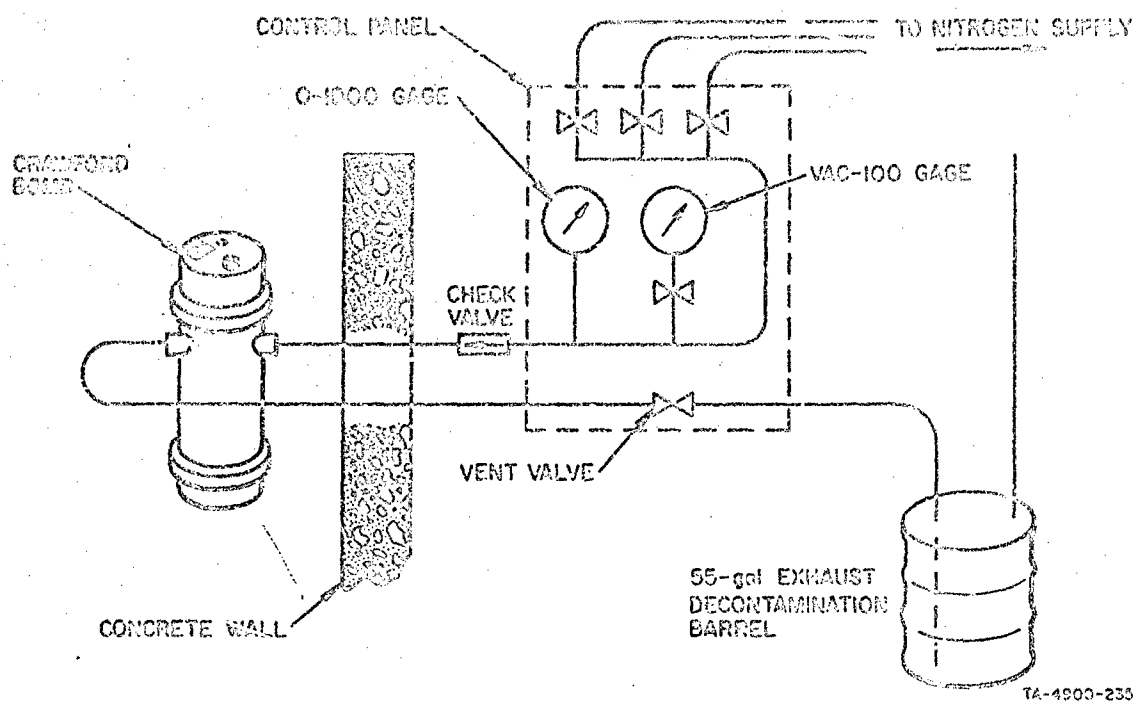


FIG. 7 SCHEMATIC OF CRAWFORD BOMB AND CONTROLS

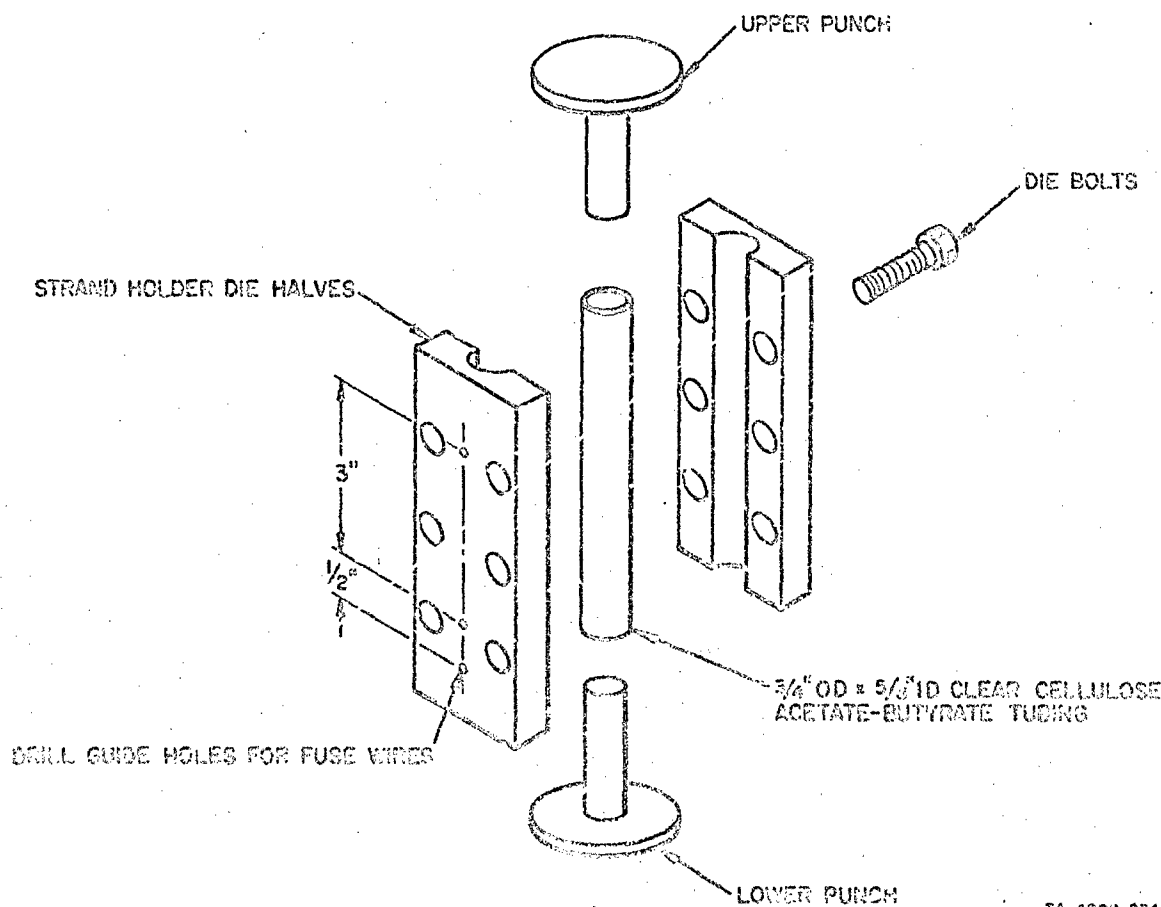
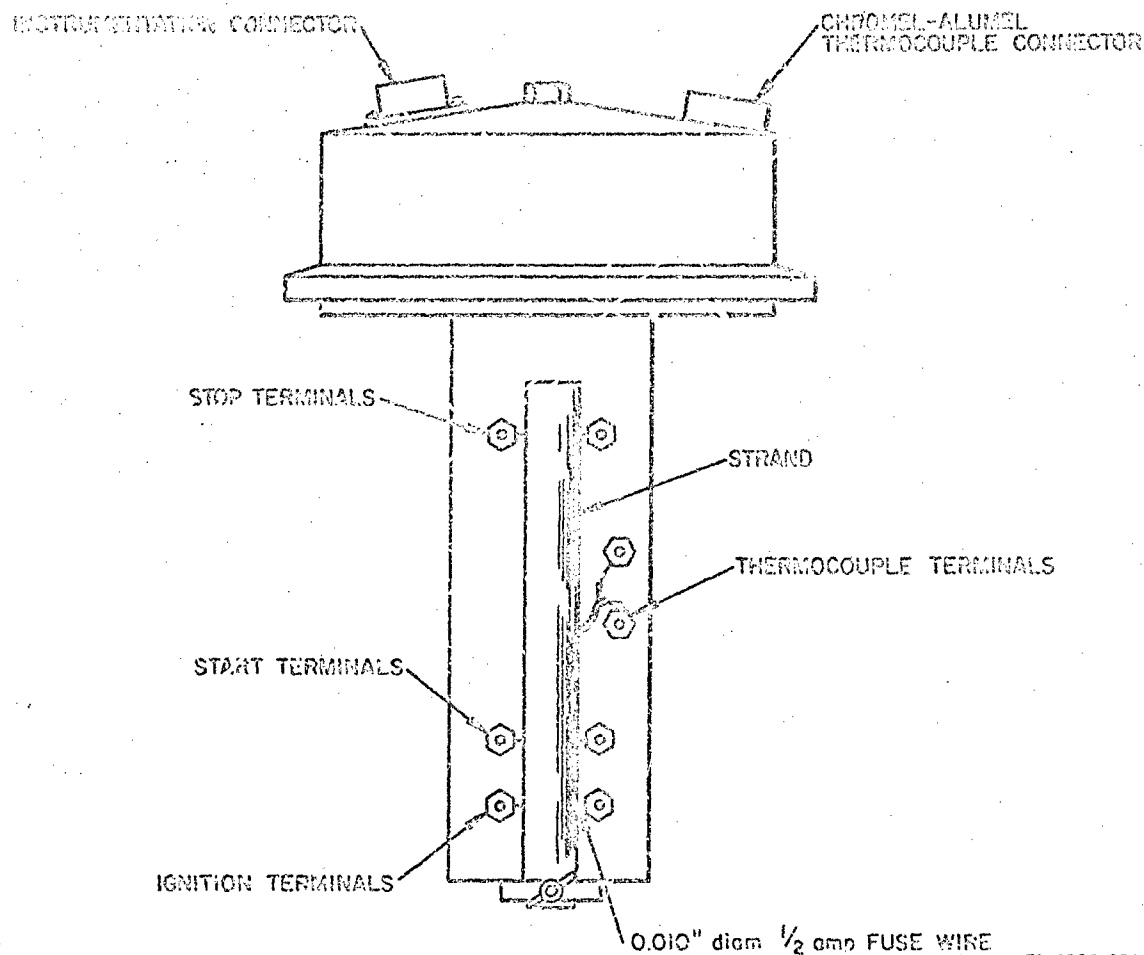


FIG. 8 STRAND FORMING APPARATUS





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FIG. 9 CRAWFORD BOMB HEAD WITH STRAND HOLDER AND INSTRUMENTATION

Figure 10 shows the burning rate-pressure relationship obtained for strands of the standard A pyrotechnic formulation pressed at 2000 psi. Also shown on the figure are data obtained at the lower pressures from hardware firings (these will be discussed in detail in a later section). The data agree within the expected scatter of these experiments and show that pyrotechnic formulations obey the familiar solid rocket propellant burning rate expression,  $r = c p^n$ . For this formulation  $c = 3.9 \times 10^{-3}$  and  $n = 0.55$ .

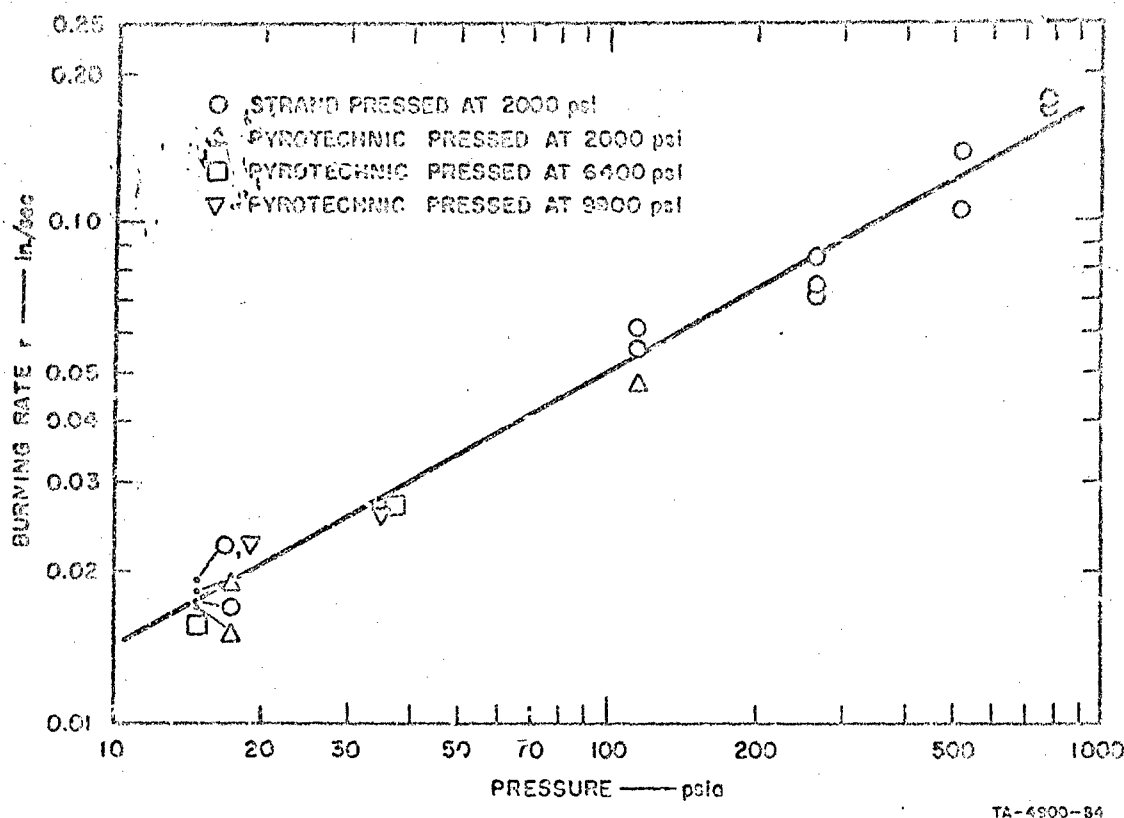


FIG. 10 BURNING RATE vs PRESSURE FOR MAA PYROTECHNIC

The MAA strand burning rate studies also illustrated the dependence of useful agent yield on combustion environment. At low pressures a thick feathery coating of red MAA condensed out on the walls of the bomb. As the pressure was raised toward 500 psi the coating became thinner and changed to an orange color, and at 750 psi the coating was completely black, indicating complete breakdown of the agent. The increased degradation is a consequence of the increased residence time in the combustion zone during burning at elevated pressures and of the increased flame temperature present at the higher pressures. No attempt was made to optimize the formulation for any given pressure.

A similar strand burning rate curve (see Fig. 11) was determined for the standard CS pyrotechnic at several values of strand forming pressure. The formulation contained 40.6% CS, 3.2% KC, 11.6% kaolin, 19.4% lactose, and 25.2%  $\text{FeClO}_3$ . Burning rate changes due to forming-pressure differences were not found to be significant as long as the charge was consolidated

lightly enough to prevent flashing either along the sides or into the body of the mixture. Such a result implies that the increase in density caused by increasing the forming pressure is offset exactly by a corresponding increase in thermal conductivity, thereby giving the same burning rate. For the CS formulation the burning rate constants are  $c = 2.45 \times 10^{-3}$  and  $n = 0.505$ .

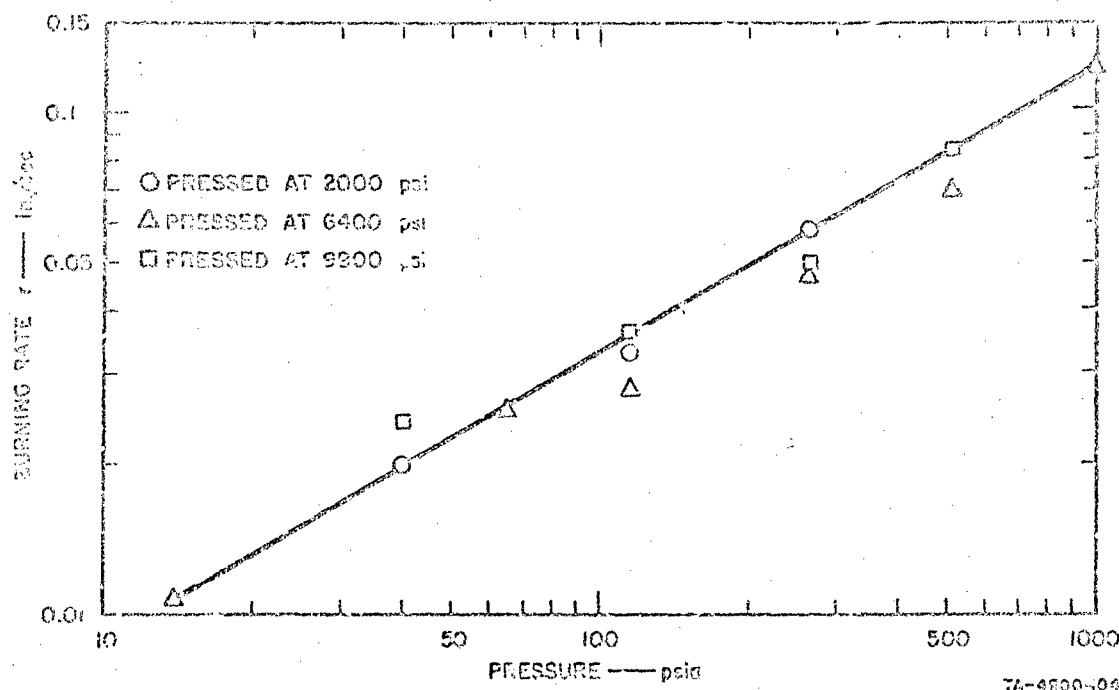


FIG. 11 BURNING RATE vs PRESSURE FOR CS PYROTECHNIC

A thermocouple was embedded in the CS pyrotechnic strands in order to obtain the maximum flame temperature as a function of operating pressure. The data obtained are shown in Fig. 12. Below 300 psia there is considerable scatter in the data, with a slight upward trend in temperature being discernible. The scatter may well be caused by poor thermal contact between the thermocouple and the pressed grain. Also the relative location of the thermocouple in the porous char bed which is formed may be an important influence on the result.

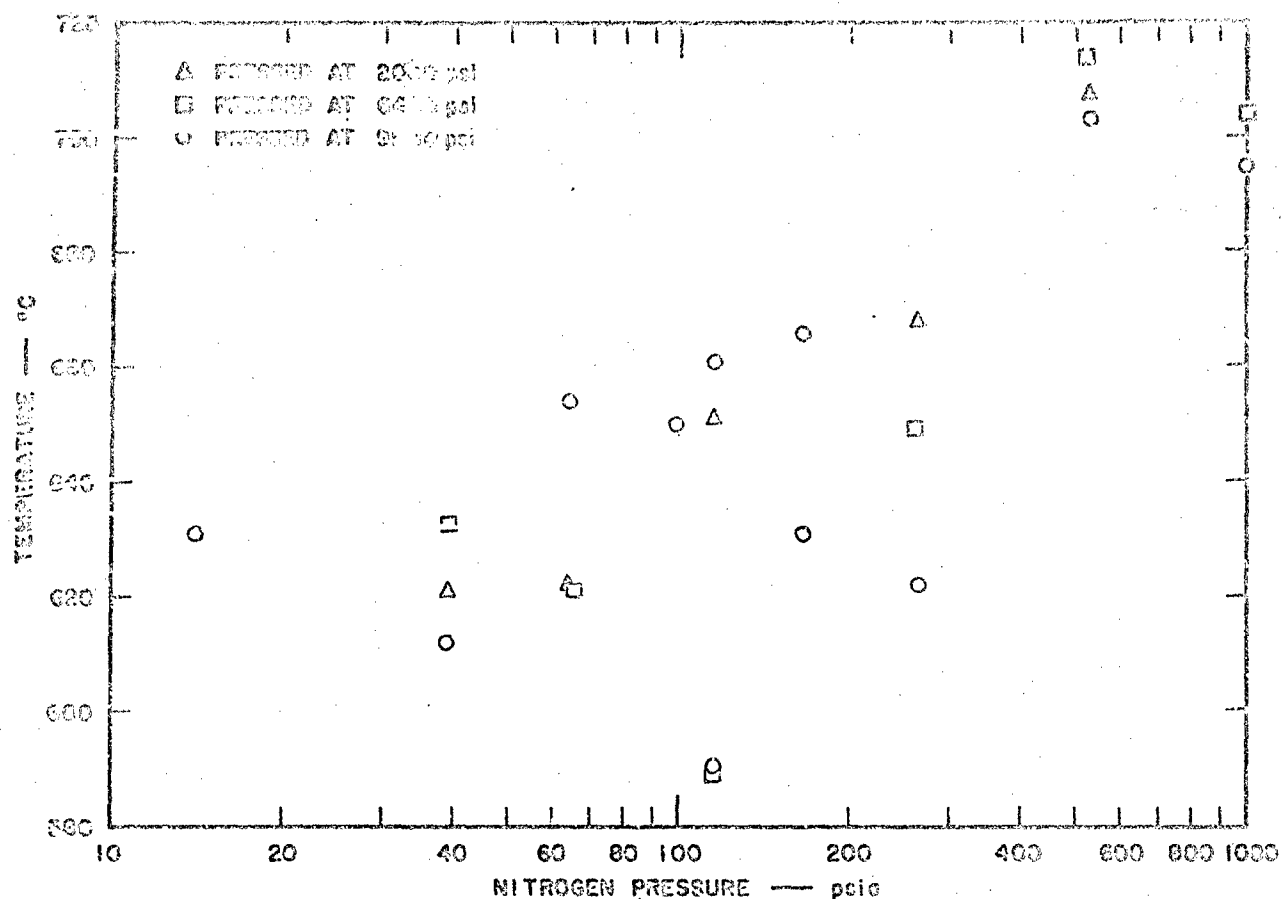


FIG. 12 PLOT OF BURN TEMPERATURE vs PRESSURE — AS MEASURED IN THE STRAND BOMB

At higher pressures, above 500 psia, the temperature appears to take a sudden upward shift. Computer calculations for the adiabatic flame temperature show an even higher value in the region of 1000 psia. Such flame temperatures are unacceptable from the standpoint of agent degradation.

Since the time that the agent spends in the high temperature flame zone is critical from the standpoint of degradation, any method that significantly increases the burning rate (and therefore decreases the residence time) without raising the flame temperature is useful. With this in mind a series of catalysts successfully used in burning rate work were evaluated. The standard mixture of 40.6% CS, 3.2% NO, 11.6% kaolin, 10.4% lactose, and 25.2%  $KClO_3$  was studied with 1% catalyst added. A summary of the test results are shown in Table III.

Table III

## EFFECT OF BURNING RATE CATALYSTS

Catalysts	Burning Rate (in./sec)
Control (no catalyst)	0.017
Copper chromite	0.013
$\text{Cu}_2\text{O}$	0.011
$\text{FeS}$	0.012
$\text{Fe}_3\text{O}_4$	0.012
$\text{MnO}_2$	0.011
Ferric octoate	0.011
Ferrocene	0.017
$\text{Fe}_2\text{O}_3$	0.012
$\text{CuO}$	0.012
Ferric acetylacetonate	0.012
Chrome green	0.013
$\text{K}_2\text{Cr}_2\text{O}_7$	0.015
N-butyl ferrocene	0.012

These results show that no burning rate enhancement is obtained; instead depression of the burning rate was common.

In view of this result, attention turned to burning rate stimulation by improved heat conduction. Revere aluminum needles (0.001 x 0.008 x 0.25 in. long) were pressed into the standard pyrotechnic at mass loading levels of one, three, and five percent. The results, shown in Table IV, indicate that the burning rate was not increased significantly by this technique. An additional modification which was tried was to slurry the basic pyrotechnic with acetone. The slurring technique permits contact between the potassium chlorate and nitrocellulose and provides an ignition train between particle agglomerates which should in principle stimulate the burning rate. A slurry containing aluminum needles was pressed into a pyrotechnic and burned, but no significant burning rate increase was obtained.

Table IV

## EFFECT OF AMBIENT PRESSURE ON THE BURNING RATE

Mass Loading (%)	Burning Rate (in./sec)
0	0.017
1	0.020
3	0.023
5	0.023

Attempts were also made to modify the burning rates by formulation changes. It was found that increases could be obtained by increasing the oxidizer-to-fuel ratio. However, this results in very high flame temperatures which would lead to significant decreases in agent yield.

Strand burning rate measurements such as those described are needed to establish the ballistic design parameters for pyrotechnic operation above ambient pressure. If the burning rate, density, burning area, and fraction of mass converted to gaseous products are known, the required orifice size to establish operation at any desired pressure can be calculated from

$$A_t = \frac{\dot{w} c^*}{P_b g}$$

where

$A_t$  = orifice area,  $\text{ft}^2$

$\dot{w}$  = weight flow,  $\text{lb/sec}$  ( $= \rho r A_b E$ )

$\rho$  = density of pyrotechnic,  $\text{lb/in.}^3$

$r$  = burning rate,  $\text{in./sec}$

$A_b$  = burning surface area,  $\text{in.}^2$

$E$  = fraction of mass converted to gaseous products

$c^*$  = characteristic exhaust velocity,  $\text{ft/sec}$

$P_b$  = burning pressure,  $\text{lb/ft}^2$

$g$  = acceleration of gravity,  $\text{ft/sec}^2$ .

The characteristic velocity  $c^*$  is given by

$$c^* = \frac{(gkRT)^{1/2}}{k \left[ (2/k+1) \right]^{1/2}}$$

where  $k$  is the specific heat ratio and  $R$  is the gas constant, both for the product gases.

For the MAA pyrotechnic  $k$  was calculated from the product gas analysis (see Section IV-A on pyrotechnic experiments) to be 1.325 and  $R$  to be 1475, giving  $c^* = 2600$  ft/sec from the above equation. This value was used to calculate orifice sizes in the pyrotechnic experiments.

Another parameter which is required for the calculation of  $A_t$  is the pyrotechnic density ( $\rho$ ) which depends upon the forming pressure. Curves of density as a function of forming pressure are shown in Figs. 13 and 14 for CS and MAA pyrotechnics. It should be noted that experience has shown that the changes in density which occur tend to be compensated for by changes in the burning rate so that the mass ejection rate per unit surface area of pyrotechnic is nearly independent of the forming pressure.

#### D. Thermal Conductivity Measurements

To support mathematical modeling studies of the combustion wave, thermal conductivity measurements have been made on both the pyrotechnic ingredients and the pyrotechnic mixes. The device used was an adaptation of the Cenco-Fitch type. Differential temperatures are measured across the specimen at regular time intervals after the material is contacted by a heat sink on one face and a heat source of a higher temperature on the other face. The slope of the curve of time versus the log of the differential emf is a measure of the thermal conductivity. Specimens were prepared using a 1-in. die. It is possible to press the sample to a relatively uniform density, since the sample thickness is only 0.5 cm. Samples studied were pressed to densities which were equal to actual pyrotechnic densities.

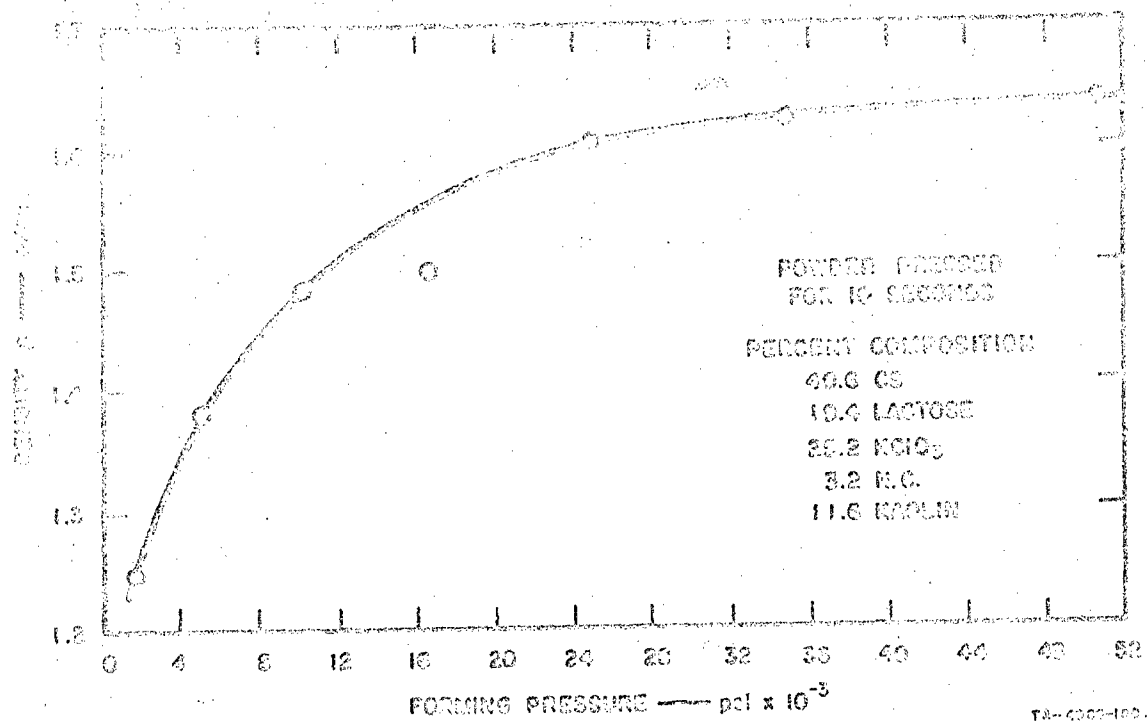


FIG. 13 DENSITY vs. FORMING PRESSURE FOR CS PYROTECHNIC

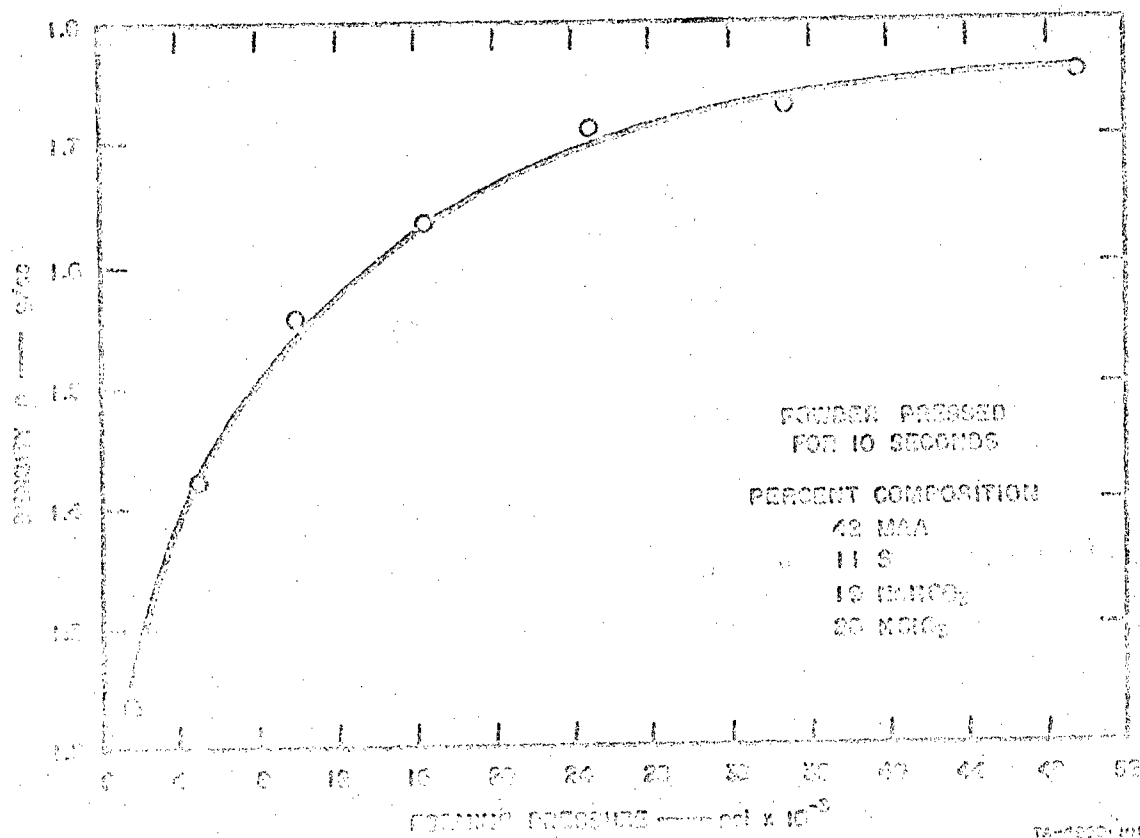


FIG. 14 DENSITY vs. FORMING PRESSURE FOR MAA PYROTECHNIC



The device (Fig. 15) is constructed so that the specimen can be placed in firm contact with all surfaces. The measuring potentiometer and null indicator are not shown. The heat source (lower block) is integral with the upper side of a pot which is heated with boiling water to ensure a constant temperature. The heat sink (upper block) is insulated by a StyroFoam ring and is backed by a low conductivity plug made of Thermobestos. A micrometer screw drive is used to bring the block down to the face of the specimen and then to compress the backing material 0.005 in. A calibrated dial on the screw is used to measure the amount of compression. A Leeds and Northrup potentiometer and an external, amplified null indicator are used to measure the emf between the thermocouples at the heat source and the heat sink.

The rate of flow of heat through the specimen is equal to the rate of heat transfer to the upper copper block (the heat sink). This can be expressed by

$$\frac{KA(T_1 - T)}{x} = Mc \frac{dT}{dt}$$

where

$K$  = thermal conductivity of the material

$A$  = area of the upper block (the specimen area is greater to minimize end effects)

$T_1$  = constant temperature of the heat source

$T$  = temperature of face of material in contact with heat sink

$x$  = thickness of the specimen

$M$  = mass of the heat sink

$c$  = specific heat of the heat sink

$dT/dt$  = rate of increase of temperature of the heat sink.

The differential emf,  $V$ , between the two thermocouples at the heat source and in the heat sink is proportional to the temperature difference, i.e.,

$$V = c(T_1 - T)$$

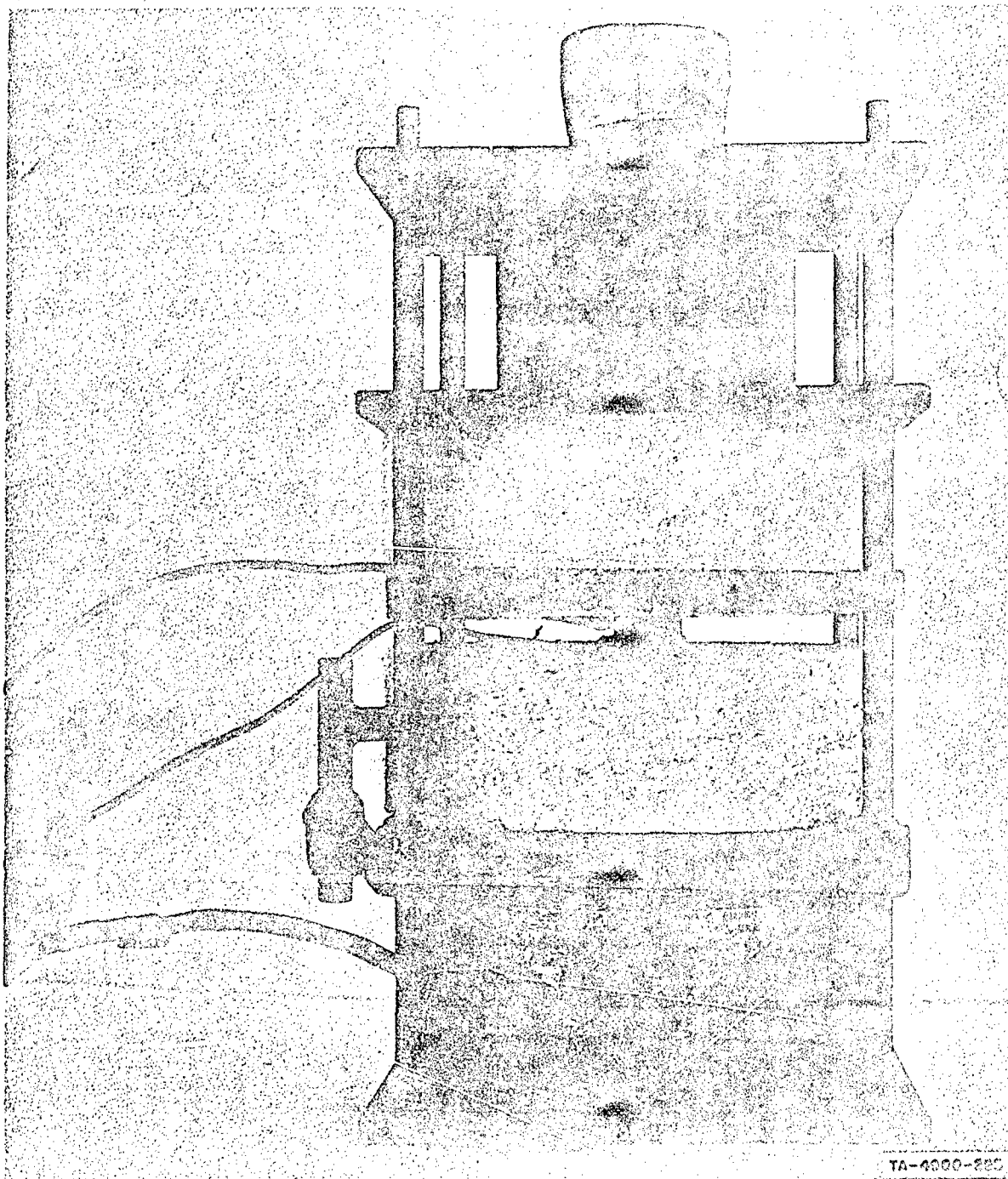


FIG. 15 APPARATUS FOR MEASURING THERMAL CONDUCTIVITY

The instantaneous rate of change in differential emf is a measure of the instantaneous rate of temperature rise in the copper block:

$$\frac{V}{dt} = -c \frac{dT}{dt}$$

Then,

$$\frac{KA\Delta V}{x} = -Mc \frac{d(\Delta V)}{dt}$$

giving

$$dt = - \frac{xMc}{KA} \frac{d(\Delta V)}{\Delta V}$$

By integration

$$t = - \frac{xMc}{KA} \ln (\Delta V) + \text{constant}$$

The substitution of initial conditions leads to the following expression:

$$t = -2.303 \frac{xMc}{KA} [\log(\Delta V) - \log(\Delta V)_0]$$

Thus the slope  $m$ , of  $t$  versus  $\log \Delta V$  can be expressed as

$$m = -2.303 \frac{xMc}{KA}$$

The constants of our apparatus are:

$$M = 81.54 \text{ g}$$

$$c = 0.093 \text{ cal/g}$$

$$A = 3.24 \text{ cm}^2$$

The thermal conductivities for the test specimens were calculated according to the above scheme. Since calibration of the equipment against a standard of known conductivity would provide a greater degree of assurance, the thermal conductivity of Lucite (Flexiglas) was also checked as a standard.

The compositions of the pyrotechnics listed in Table V were:

1. MAA pyrotechnic mix Mod 1 consisted of 42% MAA, 11% sulfur, 19% sodium bicarbonate, and 28% potassium chlorate. The ingredients were dry mixed and pressed at 6400 psi.
2. CS pyrotechnic Mod 2 consisted of 40.6% CS, 19.4% lactose, 25.2% potassium chlorate, 3.2% nitrocellulose, and 11.6% kaolin. The ingredients were dry mixed and pressed at 6400 psi.
3. CS pyrotechnic Mod 3 was slurried with 4.8 parts per hundred of acetone prior to pressing.
4. CS pyrotechnic Mod 4 was slurried with 4.8 parts per hundred of acetone with the nitrocellulose predispersed in the acetone.
5. CS pyrotechnic Mod 5 consisted of 35% CS, 30%  $\text{KClO}_3$ , 25% lactose, 10% kaolin, and 3.43 added parts per hundred nitrocellulose. One hundred grams of the CS, potassium chloride, lactose, and kaolin mix were slurried with 39 grams of acetone containing 3.43 grams of nitrocellulose in solution. The mixture was dried and then pressed: this procedure reproduced Edgewood Arsenal techniques.

It will be observed that the highest thermal conductivity of any of the pyrotechnic mixes was obtained with a mixture prepared by the Edgewood Arsenal procedure. Materials were pressed at a pressure of 6400 psi; measured densities were 1.470 g/cc for the dry mixture CS pyrotechnics and 1.455 g/cc for the slurried mix. The higher conductivity measurements can be attributed to the intimate mixing which is obtained using the slurry technique and the higher particle density which results.

#### B. Methylaminoanthraquinone (MAA) Vapor Pressure Measurements

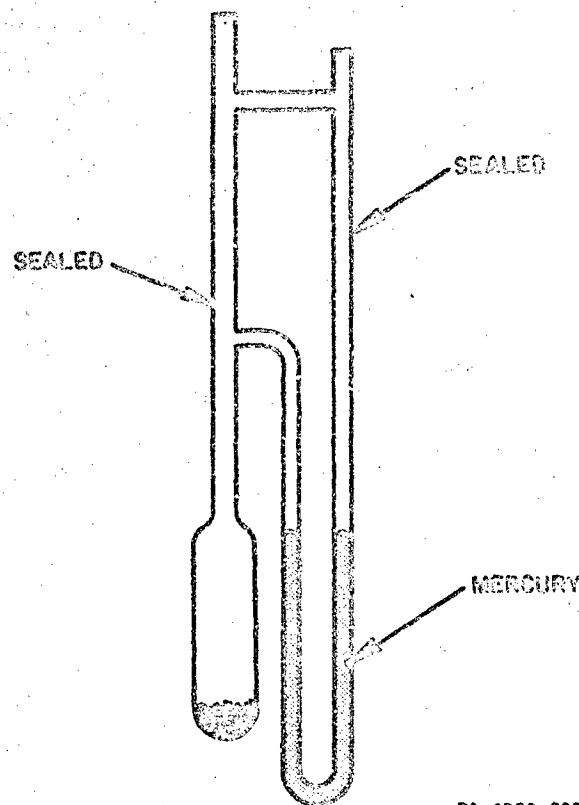
The efficiency with which an agent or its simulant is dispersed depends on its vapor pressure-temperature behavior. For this reason, vapor pressure measurements on the simulant MAA were undertaken at the direction of Edgewood Arsenal.

Table V.

THERMAL CONDUCTIVITY DATA  
FOR PYROTECHNIC INGREDIENTS AND MIXTURES

Material	Thermal Conductivity, K (g-cal-cm/ <sup>°</sup> C-cm <sup>2</sup> -sec)
Methylaminocanthraquinone (MAA)	8.515 x 10 <sup>-4</sup>
Sulfur	4.785 x 10 <sup>-4</sup>
NaHCO <sub>3</sub>	4.746 x 10 <sup>-4</sup>
KClO <sub>3</sub>	7.492 x 10 <sup>-4</sup>
CS	9.819 x 10 <sup>-4</sup>
Nitrocellulose (NC)	14.47 x 10 <sup>-4</sup>
Kaolin	19.84 x 10 <sup>-4</sup>
Lactose	10.87 x 10 <sup>-4</sup>
MAA Pyrotechnic Mod 1	11.27 x 10 <sup>-4</sup>
CS Pyrotechnic Mod 2	11.54 x 10 <sup>-4</sup>
CS Pyrotechnic Mod 3	13.48 x 10 <sup>-4</sup>
CS Pyrotechnic Mod 4	13.11 x 10 <sup>-4</sup>
CS Pyrotechnic Mod 5	15.14 x 10 <sup>-4</sup>
Lucite Control	6.703 x 10 <sup>-4</sup>

Initially an attempt was made to determine the vapor pressure of technical grade MAA obtained from McKesson and Robbins. This material was found to be highly impure, and some decomposition or charring occurred when the material was dried under vacuum at 90°C. The impurities evidenced themselves by the residual gas pressure left in the isotensiscopes (Fig. 16) after cooling. A second experiment, this time with material obtained from American Cyanamid, was performed, and again the material was dried at 90°C under vacuum. Decomposition still occurred, with some charring at the melting point and above.



VA-12000-223

FIG. 16 ISOTENSISCOPE

It was apparent from this preliminary work that any material which was to give accurate values for the vapor pressure needed purification. This was accomplished in the apparatus shown in Fig. 17. The American Cyanamid HMA was loaded into bulb 1, through arm A, which was then sealed off. The bottom half was heated to 185° C while evacuating through C; the sample was sublimed, and distilled (above melting point) into bulb 2. A charred deposit remained in bulb 1; this section and arm C were then sealed off from the rest of the tube. In a similar way, the sample was pseudo-distilled into bulb 3 at 185° C leaving negligible residue, and bulb 3 was completely sealed off while under a vacuum of  $2 \times 10^{-3}$  torr.

The purified material was subsequently distilled into D and E at 185° C. Part of the HMA obtained in this manner was very dark; it is uncertain whether this was a result of decomposition or transferred contamination; the dark color may have simply been produced by the state of subdivision which existed. In any event, that section of E containing

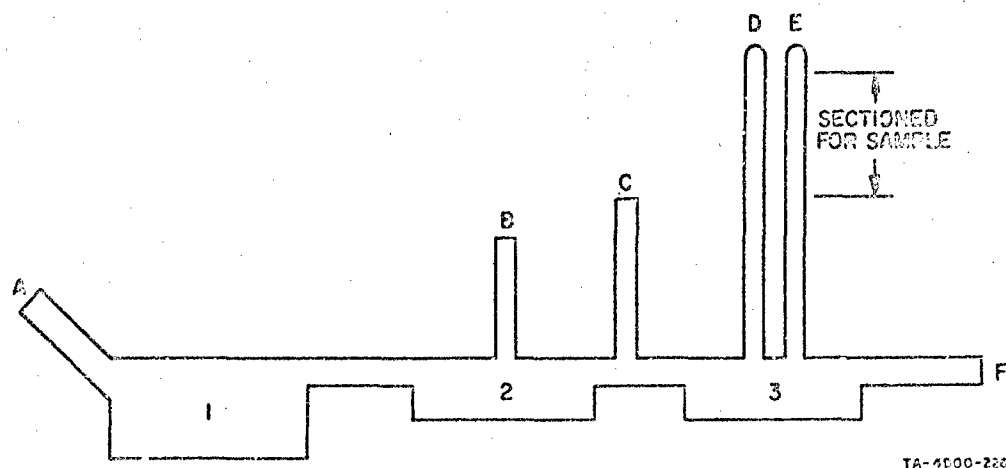


FIG. 17 SUBLIMATION — DISTILLATION TUBE

the material with the least dark coloration was sectioned off and dropped directly (Pyrex and sample both) into a third and smaller isotenscope. The measured vapor pressure of this material is listed in Table VI and shown in Fig. 18.

Compared to transpiration and Rodebush methods of measuring vapor pressure, the isotenscope technique is ideal for detecting decomposition in the suratmospheric range. However, in this particular case, the vapor pressure of the compound is very low at relatively high temperatures so that the precision of the measurements can be adversely affected by any temperature gradients which may develop in the mercury column. This fact can be better appreciated when one compares the vapor pressure of the liquid with the vapor pressure of mercury over the range investigated. The vapor pressure of mercury rises from 6 mm, at the melting point of MAA, to 80 mm at the highest experimental temperature. At the higher temperatures, a gradient of  $1/2^{\circ}\text{C}$  across the columns of mercury will produce a pressure difference of 1 mm, due to mercury alone. It is suspected that the two measured values which lie well above the curve in Fig. 18 (at  $214.3$  and  $222.8^{\circ}\text{C}$ ) were produced by such a gradient.

The general agreement of the experimental data would appear to establish their validity; but, in light of the above discussion, it may be wise to consider verifying these results by an alternative technique.

Table VI  
EXPERIMENTAL VAPOR PRESSURE OF PURE MAA

Temperature (°C)	Pressure (mm Hg)	1000/T (T in °K)	Log <sub>10</sub> p (p in mm Hg)
346.7	(0.09)	2.865	No data interpretation because of experimental scatter.
373.2	(0.10)	2.632	
399.1	(0.16)	2.543	
414.0	(0.17)	2.416	
428.4	(0.21)	2.369	
435.0	(0.31)	2.298	
445.8	0.27	2.242	-0.5686
447.0	0.28	2.236	-0.5528
457.4	0.46	2.185	-0.3372
468.3	0.84	2.137	-0.0757
468.8	0.82	2.135	-0.0862
477.0	1.24	2.096	0.0934
478.0	1.30	2.087	0.1139
487.5	3.00	2.054	0.4771
488.0	3.67	2.017	0.5647
477.5	1.26	2.097	0.1004
486.9	1.75	2.055	0.2430
488.5	2.58	2.015	0.4116
500.8	4.03	1.972	0.6953
517.9	6.23	1.931	0.7945
526.6	10.10	1.899	1.0043
446.6	1.85		2.672
466.5	1.80		2.553



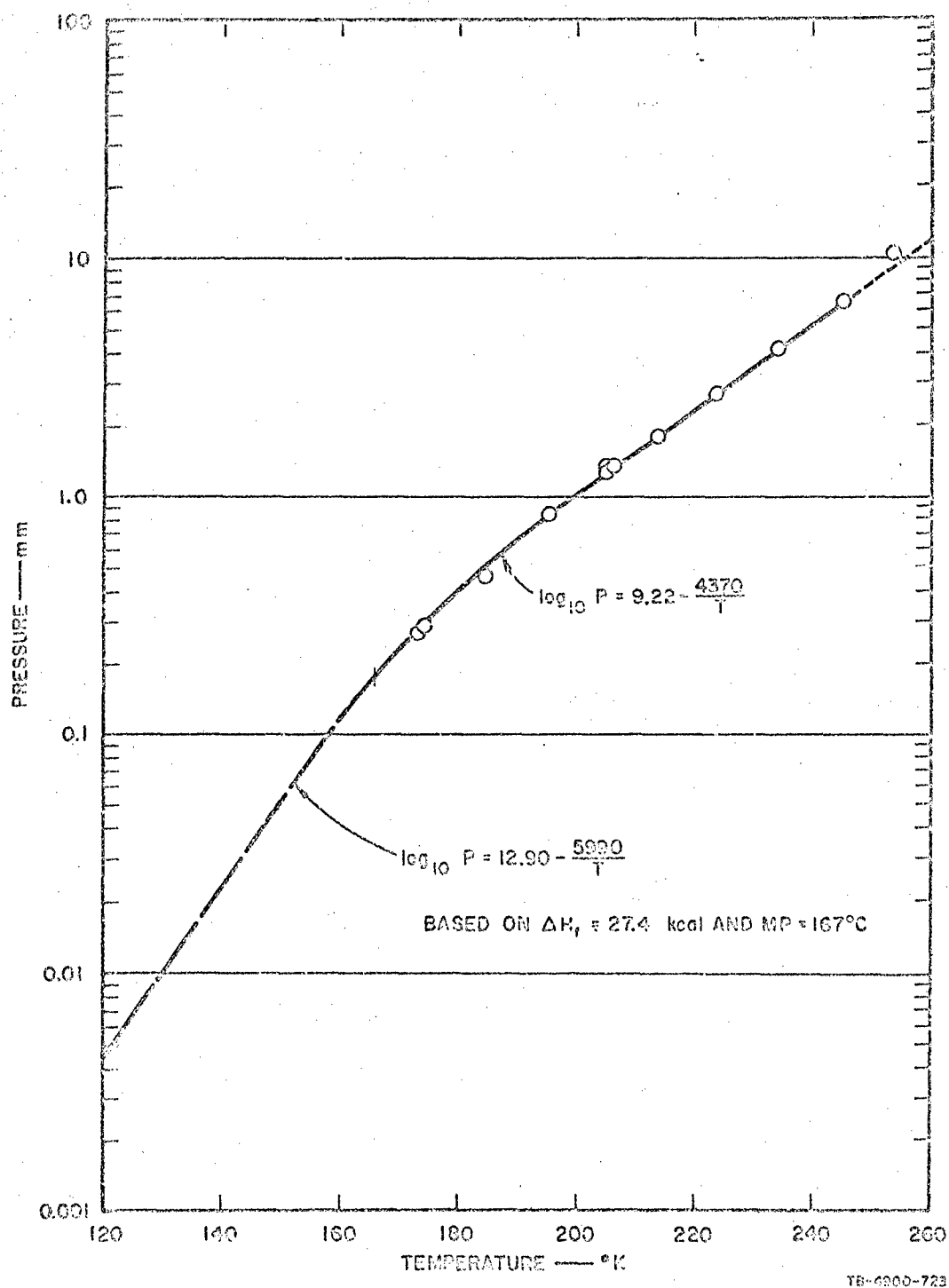


FIG. 10. PRESSURE vs. TEMPERATURE FOR 1-METHYLAMINOANTHRAQUINONE

The vapor pressure curve can best be represented (neglecting scatter) by the equation:

$$\log p = 9.2234 - \frac{4370}{T}$$

where p is the pressure in millimeters of mercury and T is the temperature in degrees Kelvin.

The heat of vaporization calculated from the slope of this line is 20.0 kcal. This value appears to compare well with the heat of sublimation value measured by Beynon and Nicholson<sup>14</sup> of 27.4 kcal. Comparing these values with similar values for the parent compound anthraquinone, where  $\Delta H_g = 25.2$  kcal and  $\Delta H_v = 15.8$  kcal, the agreement in trend is reasonably good.

Beynon and Nicholson's value and the extrapolated vapor pressure at the melting point were used to calculate the sublimation vapor pressure curve shown in Fig. 18. If the data are extrapolated to provide a vapor pressure of one atmosphere, the corresponding temperature is 416°C.

Although the data do not provide complete information over the range of pyrotechnic operating temperatures, extrapolation of the data is practical up to the point of decomposition of the MAA. There is some evidence of MAA decomposition at the temperatures already achieved, but by using one of the other techniques available, such as the transpiration method (up to 300°C) or the pyro-gauge technique (500-600°C), the vapor pressure can be measured at much higher temperatures.

#### IV PYROTECHNIC EXPERIMENTS

In order to properly identify the critical processes occurring during combustion of a pyrotechnic, it is imperative to obtain a careful material balance before and after combustion. An experimental study of the combustion wave itself is also important because the product gases formed in the flame zone and in the ash bed provide the environment in which the agent must survive to become a useful aerosol.

##### A. Mass Balances on Pyrotechnics

In the past nearly all quantitative pyrotechnic output data have been obtained from aerosol chambers. The technique incorporates a large chamber which is continuously stirred by a fan. A pyrotechnic is fired or burned in the chamber. The fan is started before the pyrotechnic is fired and continues after the firing has ceased until sampling is complete. Samples of aerosol are taken from the tank at intervals of time. A carefully measured one-liter sample of aerosol is passed through a total filter, and the filtrate is used for agent analysis. The sampling is done periodically for several minutes, and the concentration of agent in the tank is then plotted as a function of time. The values obtained are extrapolated back to zero time to estimate the initial concentration. This concentration is then taken as the true output of the pyrotechnic.

Wind tunnels have also been used for output measurements. Wind tunnel measurements require a well-mixed, uniform flow of aerosol, and the technique may be quite effective if the aerosol flow through the test section is homogeneous and if continuous sampling is used. In general, however, despite careful calibration, precise measurements are difficult by either of the above methods. Using chamber or wind tunnel techniques, mass balances of pyrotechnics are very difficult to obtain.

In our work here at the Institute it was decided to use a total sampling technique by capturing all of the output from a given pyrotechnic and performing suitable chemical analyses upon it. Preliminary experiments were carried out using a 50-gallon steel tank; a pyrotechnic was burned and the combustion products were collected in the tank. The gas was sampled for mass-spectrographic analysis, and the aerosol was extracted by washing the tank down with suitable solvents. It was found, however, that this process was very time-consuming, and with small samples the repeatability of results was poor. If an inert gas was present in the tank, the gas analysis was found to be inaccurate, apparently because of dilution. Accordingly, while this experimental procedure may be suitable for very large devices, an alternative approach is needed for evaluating small-scale pyrotechnic compositions in the laboratory.

Since it was desirable to improve on the tank technique, several other methods were evaluated. In one approach the pyrotechnic was burned and the products of decomposition were collected in a five-liter three-neck flask. In another approach the products of decomposition of the burning pyrotechnic were used to inflate a plastic bag. The first method suffers from the inherent disadvantage that the pressure in the flask increases during burning, and this may result in a variation in burning rate and decomposition products of the pyrotechnic; nevertheless, useful information on the burning of CS pyrotechnics has been obtained using this method. Both methods enable the amount of noncondensable gases produced to be readily determined by measurement of the pressure rise.

The complete five-liter glass receiver test assembly is shown in Fig. 19. The pyrotechnic canister (shown in Fig. 20) held up to 25 grams of mixture. The system was arranged to allow the pyrotechnic to discharge either into a vacuum or into a helium atmosphere. If the test was fired into air, gas analysis was unreliable because of the mixing and possible further chemical reaction between the combustion products and the oxygen and nitrogen of the air.

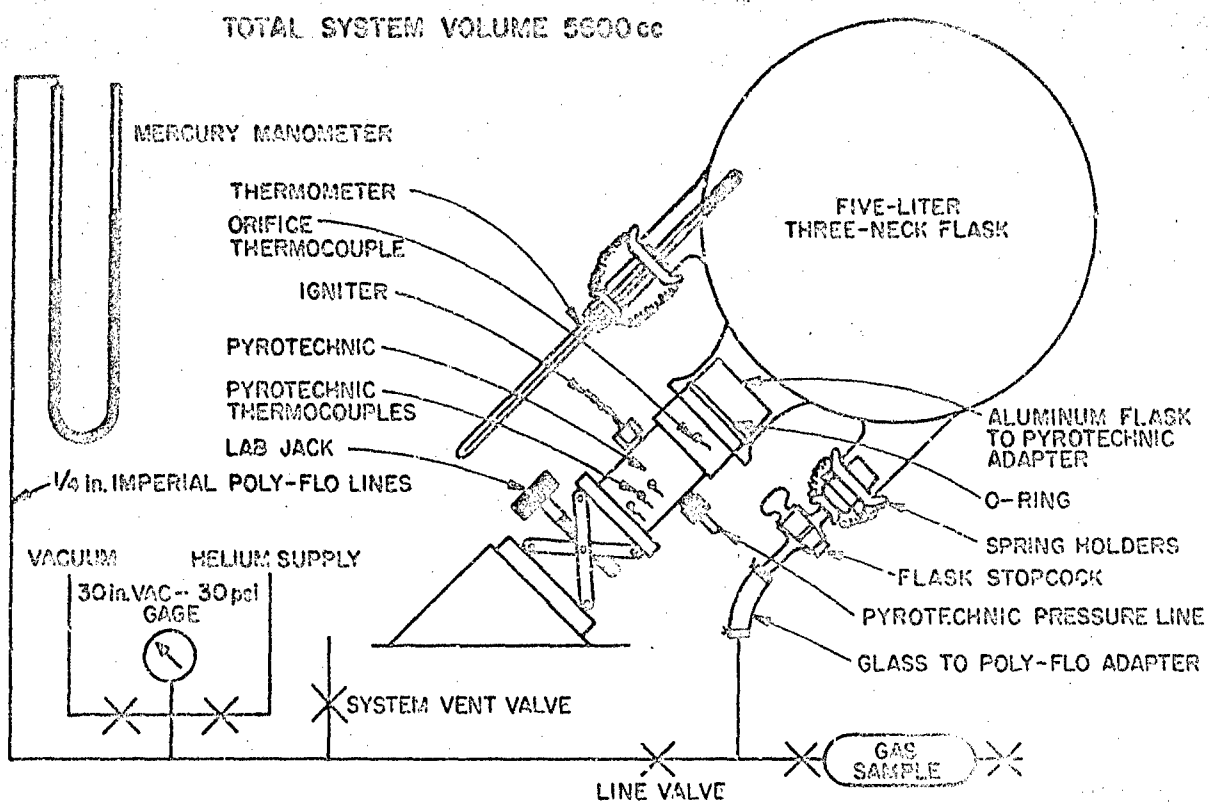


FIG. 19 GLASS RECEIVER — PYROTECHNIC BURNING SYSTEM

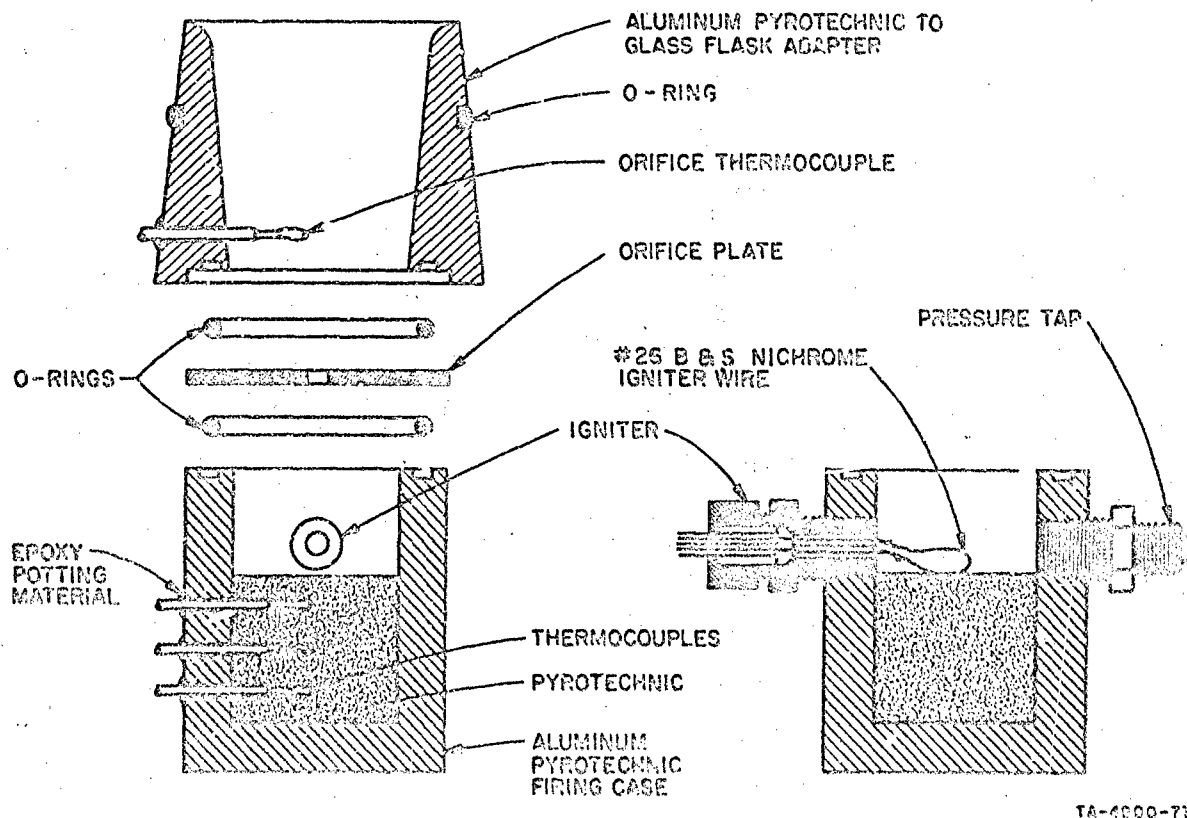
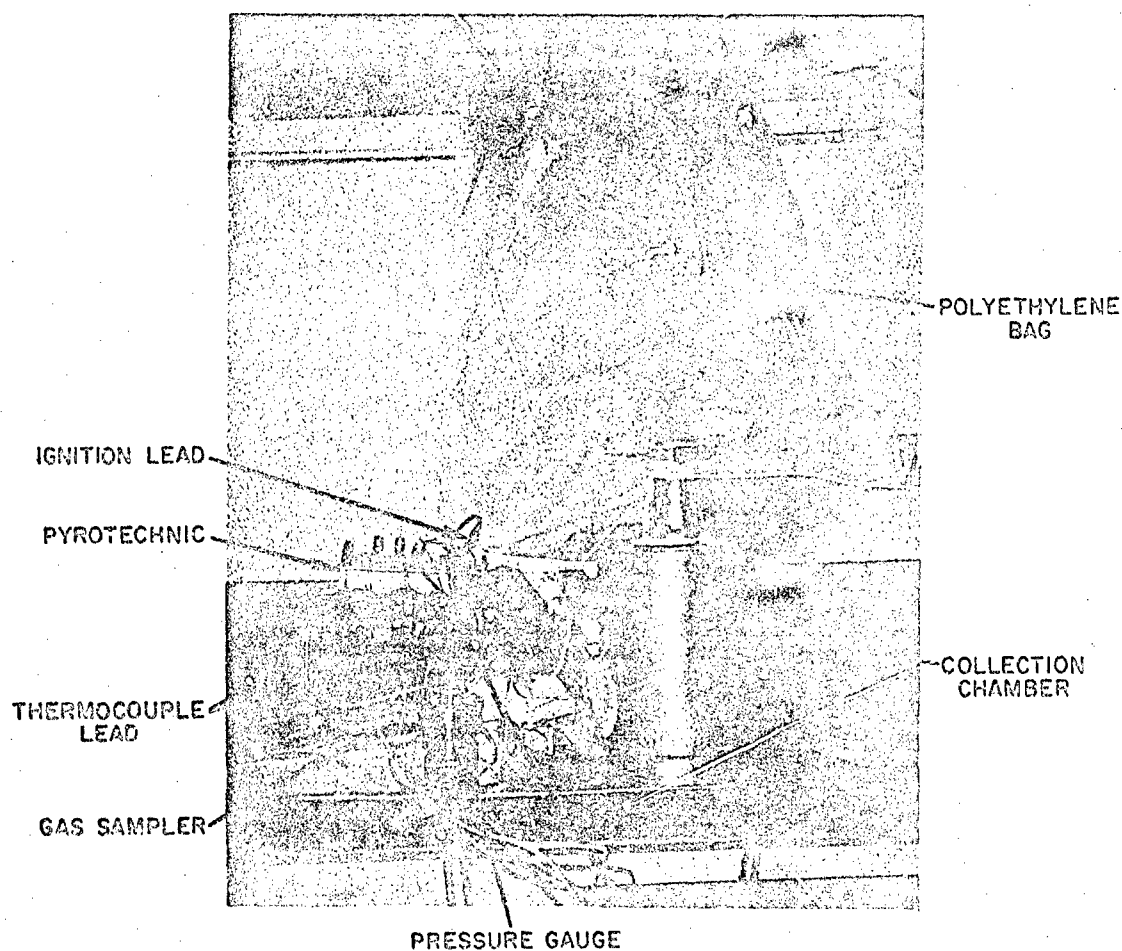


FIG. 20 PYROTECHNIC CANISTER ASSEMBLY

A larger aluminum canister was also designed for pyrotechnic composition studies. Its dimensions, 5.85 cm in diameter and 11.91 cm deep, were selected to duplicate as nearly as possible the sizes used for the service grenade. The canister was fitted with several adaptors for the gas sampling lead, the thermocouple leads, the pressure gage lead, and the inert gas purge lead. Wires were attached for hot-wire ignition. Pyrotechnic mixes were pressed directly into the canister in five increments to give uniform pressing density. For total recovery tests, the pyrotechnic was fired horizontally into a closed container fitted with a polyethylene bag to collect the gases without a pressure rise (see Fig. 21). If it is deemed necessary, the whole unit can be evacuated and then purged with helium to reduce contamination by air.



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FIG. 21 PYROTECHNIC TEST ARRANGEMENT USING POLYETHYLENE BAG FOR GAS COLLECTION

The use of a polyethylene bag for collection of the by-products offers several advantages. Contamination is kept to a minimum when using agents. The polyethylene bag is kept flat and a vacuum may be pulled on the system to minimize air or helium contamination of gas samples. All of the products are collected and gas output may be easily determined without back pressure on the pyrotechnic during operation.

This system of recovery of agent has some significant advantages over conventional chamber or wind tunnel techniques. No extrapolation of the data is needed since actual agent concentrations are measured directly. Its largest single drawback is that little can be learned of particle size and cloud duration. The cloud particle size is readily determined via impact samplers or through settling studies in a chamber. From our experience the most important aspect of agent-generating pyrotechnics is agent survival through the pyrotechnic. If the agent survives and is expelled to condense outside the pyrotechnic, its particle size will probably be small enough to remain dispersed as an aerosol. We have not seen exceptions to this, though exceptions may exist.

A determination of the ingredients which are discharged as a gas or remain as residue in the pyrotechnic is only representative of the information really desired, since on cooling the by-products from the pyrotechnic, the equilibrium is shifted and the compounds which existed at high temperatures are no longer the same as those analyzed. A direct analysis of the gases and solids which are present during combustion would be ideal, but in lieu of this impracticality an estimate of the actual products must be made from the data which are available.

The formulation selected for the study of MAA-based pyrotechnics consisted of 42% MAA, 28%  $\text{KClO}_3$ , 11% sulfur, 19%  $\text{NaHCO}_3$ . In the initial studies, the pyrotechnic was burned in a heavy-walled aluminum canister with the gases being collected in a polyethylene bag; after burning, the volume of the noncondensable gas generated was measured by a water-displacement procedure, and a sample of the gases was collected in an evacuated stainless steel cylinder for mass-spectrographic analysis. The burning

temperature was determined by the use of a thermocouple which was pressed into the pyrotechnic during loading of the canister, while the burning time was obtained by visual observation of gas emission from the canister.

Methylene chloride was used as a wash for the hot gases from the pyrotechnic. The gases from the pyrotechnic were discharged below the liquid level in the receiver and were forced through the solution. Methylene chloride is very stable and no reaction with the pyrotechnic gases was observed. An additional advantage to the use of methylene chloride was the ease with which a collected sample could be concentrated. Overnight storage in the hood usually allowed a sample to be concentrated to a solid. Care was exercised to prevent contamination of the gas samples by the collection solvent.

In analyzing noncondensable gases by mass-spectrographic methods, it was found that the methylene chloride vapor and helium interfered with accuracy of gas analysis, so the gas samples for this purpose were drawn directly from the pyrotechnic device into an evacuated glass cylinder. A remotely operated, normally closed solenoid valve was used for sampling the gas. The glass cylinder was attached to the valve and the system was evacuated to a very low pressure--during the test the solenoid valve was opened allowing the gases from the pyrotechnic to be forced into the glass sampler. All controls and recording instruments are located some 30 ft from the device and are protected by a transparent protective shield. Pyrotechnic pressure and temperature measurements were recorded on a 12-channel Visicorder which was operated with a chart speed of  $\frac{1}{2}$  to 1 in./sec. The galvanometers were calibrated to give maximum deflection on 8 in. paper for expected temperatures and pressures.

After firing, the gas sample was removed for analysis and ash samples were recovered from the pyrotechnic. The ash was ground in a standard laboratory grinder to a fine powder and suitable aliquots were weighed for analysis. Any agent (or simulant) deposited outside the orifice of the pyrotechnic device was washed into the methylene



chloride; the bag was similarly washed. As a check, the volume of gas generated was measured on several occasions by eliminating the use of methylene chloride and simply determining the volume of the gases in the bag after cooling.

The pertinent experimental details for two test burnings, runs B-2 and B-3, are given in Table VII. Mass-spectrographic analysis of the noncondensable gases was carried out for pyrotechnic runs B-2 and B-3, and a conventional inorganic wet analysis was also performed on the solid residue. The data from these analyses are given in Table VIII. Some care must be taken in the interpretation of these results because of the large amount of unidentified material.

The results shown in Table IX indicate that the coolant, sodium bicarbonate, produces a significant amount of carbon dioxide and that the chief volatile products formed from the sulfur are traces of  $\text{CS}_2$  and  $\text{COS}$ . The wet analysis performed on the residue in the canister reveals that the chlorate ion is being converted in the combustion process to both chloride and perchlorate, and that the sulfur is oxidized primarily to sulfate.

Since techniques for comprehensive analysis of the suspected combustion products were not previously available, it was necessary to develop suitable procedures. On the basis of X-ray analysis of by-products of pyrotechnic residue, it was reported earlier that some sulfonation of the MAA ring structure may have been taking place. Chemical analysis shows this to be untrue--the MAA ring structure is remaining intact. However, elemental sulfur and the elemental carbon have both been found in significant quantities; thio-type compounds appear to be probable constituents of both by-products.

Mr. Diener of Edgewood Arsenal pointed out that many of the sulfur compounds formed during the burning of the pyrotechnics may be sensitive to moisture. To ascertain whether this was an important factor, a pyrotechnic was subsequently burned in a dry box under a blanket of helium and the solids collected from both the gas phase and the ash. These samples, thought to contain moisture-sensitive thio-carbonates and other sulfur compounds, were then analyzed.

Table VII

## HAA-CONTAINING PYROTECHNIC MATERIAL BALANCE

Parameters	Test B-2	Test B-3
Forming pressure (psia)	19,100	6,375
Pyrotechnic density, g/cc	1.625	1.37
Weight of pyrotechnic (g)	22.6	13.3
Length (cm)	2.74	1.92
Burning time (sec)	56	45
Gas volume corrected to 0°C and 1 atm (liters)	2.9	2.10
Weight of residue (g)	11.8	7.1
Weight of gas (g)	5.42	3.9
Weight of aerosolubilized material (g)	6.0	2.3
Burning rate (cm/sec)	0.0427	0.0425
Burning pressure (mm Hg, gage)	5	2
Temperature in pyrotechnic (°C)	555	525
Temperature in orifice (°C)	325	380
Burning surface area (cm <sup>2</sup> )	5.06	5.06
Average molecular weight of gases	40.7	40.9
cc gas generated/g pyrotechnic burned	123	153

Table VIII

## WET ANALYSIS DATA FOR THE SOLID PHASE

Species	Test B-2 (wt %)	Test B-3 (wt %)
$\text{Cl}^-$	3.8	10.4
$\text{ClO}_4^-$	11.2	2.8
$\text{SO}_3^-$	---	0.1
$\text{CO}_3^-$	3.5	2.7
$\text{SO}_4^{=}$	11.0	12.4
$\text{K}^+$	19.6	14.9
$\text{Na}^+$	<u>6.6</u>	<u>10.5</u>
	60.7	53.8
Unidentified material	39.3	46.2

Table IX

## MASS-SPECTROGRAPHIC DATA FOR THE GAS PHASE

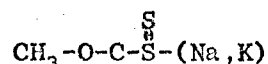
Component	Test B-2 (mole %)	Test B-3 (mole %)
$\text{CO}_2$	71.0	77.0
A	--	0.1
$\text{COS}$	1.3	1.2
$\text{CS}_2$	1.5	0.6
$\text{H}_2$	0.5	0.7
$\text{H}_2\text{O}$	1.3	1.1
$\text{N}_2$	3.4	7.1
$\text{CO}$	8.9	3.2
$\text{O}_2$	<u>12.2</u>	<u>9.0</u>
	100.1	100.0

Methylaminoanthraquinone is insoluble in water, whereas a sulfonated methylaminoanthraquinone is water soluble. Accordingly, aliquot portions of the ash and the condensed vapor were extracted repeatedly with hot water. The filtrate was then treated with 2M NaOH and then with  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_4$ . Development of a pink color would have indicated the presence of sulfonated MAA. The procedure was tested using sodium methylanthraquinone sulfonate as a sulfonated substitute for sulfonated MAA and a bright color was developed. The test was negative for both ash and vapor, indicating no sulfonation.

The literature<sup>13</sup> describes a potentiometric titration for estimating thiocarbonates quantitatively in the presence of sulfide, xanthates, chlorides, and carbonates. The apparatus employs a silver wire electrode and a calomel reference electrode.

A titration curve which was obtained using this procedure is shown in Fig. 22. The inflections which appeared differ slightly from those reported previously, but some observations can be made:

1. Inflection No. 1 is near that which has been attributed to sulfide. If it is due to sulfide, it represents about 1% by weight of the ash as sodium or potassium sulfide.
2. Inflection No. 2 is near that which has been attributed to trithiocarbonate ( $\text{CS}_3=$ ). If it is due to trithiocarbonate, it represents about 7% by weight of the ash as sodium or potassium trithiocarbonate.
3. Dithiocarbonates are reported as being unstable in solution and would not be expected to be titrated. Monothiocarbonates are not discussed.
4. The broad No. 3 inflection occurs at an emf which has been attributed to sodium xanthate-cellulose complexes.<sup>15</sup> It is conceivable that a xanthate-like complex could be formed, during pyrolysis, of the structure



If this is the actual source of inflection No. 3, it represents about 8 to 9% by weight of the ash as sodium or potassium salt.

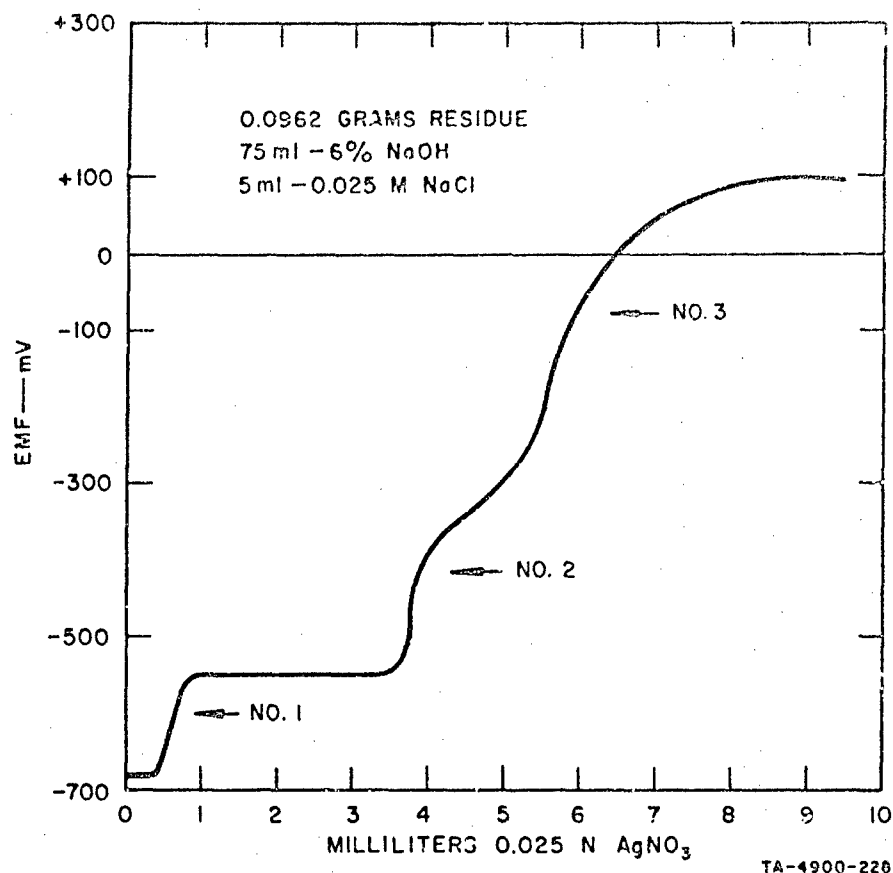


FIG. 22 TITER OF PYROTECHNIC RESIDUE

While the titration curve is quite interesting, it must be noted that it does not establish the identity of the substances being titrated. Actual identification of the pyrolysis products is possible by chemical analysis. However, this would be quite expensive and does not appear to be justified for an MAA pyrotechnic which is only a simulant.

The exact role of sulphur in the operation of the pyrotechnic remains in doubt. The appearance of small amounts of  $\text{CS}_2$  and  $\text{COS}$  in the vapor phase of the generated material indicate that the sulphur acts in part as an oxidizer in the reactions.

The appearance of  $\text{CS}_2$  and  $\text{COS}$  is not surprising, since  $\text{CS}_2$  is manufactured by heating carbon and sulfur in an electric furnace or by

reaction of methane with sulphur vapor. Carbon oxysulfide is prepared by the reaction of carbon disulfide with sulphur trioxide to produce COS and SO<sub>2</sub> or by direct reaction of carbon monoxide with sulphur or by reaction of water vapor with carbon disulfide at temperatures below 400°C. The production of these compounds, however, is indicative of the reducing atmosphere existing in this pyrotechnic mixture.

The production of measurable quantities of KClO<sub>4</sub> in the ash was rather surprising, so further tests were made. It was found that the larger pyrotechnics did not produce a measurable amount of KClO<sub>4</sub> and that all of the original KClO<sub>3</sub> could be accounted for by the KCl present in the ash. The fact that KClO<sub>4</sub> is not generated in the larger pyrotechnics is probably due to more efficient combustion and the slightly higher temperatures that result.

A typical analysis of the reaction products for a standard mixture of 40.6% CS, 25.2% KClO<sub>3</sub>, 11.6% kaolin, 3.2% NC, and 19.4% lactose was obtained by application of the total collection technique. An end-burning pyrotechnic unit containing 223.5 grams of pyrotechnic mixture was burned and all solids and gases collected for analysis. No methylene chloride was used for gas cooling and the unit was thoroughly purged with helium before the test. The average burning rate, determined from the length of the charge and the burn time, was 0.031 cm/sec or 0.012 in./sec. The final volume of the gas on cooling was 6.82 liters or 0.241 ft<sup>3</sup>.

The effective CS discharged was 57%. This does not necessarily imply that all of the CS discharged was in aerosol form, since some CS would be expected to be lost by condensation on the orifice plate. It is therefore estimated that 57% is the highest possible figure which could be considered for the effectiveness of this particular configuration. Table X summarizes the analytical results and calculations.

A preliminary balance of the chloride ions indicated that a significant amount of the chlorine was not accounted for. Accordingly, the data and procedures were re-examined. The analysis performed on the ash necessarily uses a variety of analytical procedures, and it

Table X  
SUMMARY OF ANALYTICAL DATA FOR CS PYROTECHNIC  
(End Burning Design)

	Composition of Pyrotechnic (g)	Composition of Products	
		Residue (g)	Gas (g)
CS	90.7	22.5	51.6
KClO <sub>3</sub>	56.2		
Lactose	43.5		
Kaolin	25.9		
Nitrocellulose	7.2		
Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>		21.4	
KCl		31.2	
KClO <sub>3</sub>		10.1	
C (free solid)		4.3	
H <sub>2</sub> O (calculated from lactose and kaolin)			29.4
H <sub>2</sub>	} mass-spectrographic ratios used to es- timate relative amounts		0.03
N <sub>2</sub>			0.27
CO			19.4
CO <sub>2</sub>			29.50
CHCl <sub>3</sub>			0.45
C <sub>2</sub> H <sub>2</sub> (CN) <sub>2</sub>			0.81
C <sub>6</sub> H <sub>5</sub> Cl			0.09
HCl (preliminary determination by base titration)*			<u>4.45</u>
Total Analytical Estimates		89.5	136.00
Measured Weights	223.5	89.85	133.45

\*May be subject to correction for trace quantities of CO<sub>2</sub> and for chlorobenzoic acid.

has been observed that the anion assay is usually higher than the cation assay which implies that some HCl may have been absorbed on the kaolin residue. Interpretation of the ash analysis suggested that HCl must be produced; and in addition, the computer predicted its existence in the combustion products. (The gas analysis procedure does not permit

HCl determination, since HCl is absorbed by the water formed in the combustion process.) In a separate experiment the ash was dissolved in water and found to be only slightly acidic. The gas from a duplicate pyrotechnic was bubbled through the water and the water was filtered twice to remove any traces of solids. The water (pH = 1.8) was then titrated using a standard NaOH solution. A quantitative analysis of  $\text{Cl}^-$  has conformed that the principal acid is HCl. The water was found to be slightly more acidic than could be accounted for by the missing chlorine. Trace quantities of dissolved  $\text{CO}_2$  and orthochlorobenzoic acid (not identified so far) may contribute to the total acidity.

The pyrotechnic ash sample was washed to remove all water-soluble materials and was then fired at  $850^\circ\text{C}$  to remove all traces of organic materials. The material remaining should be kaolin residues less the bound water; this was found to yield 102% of the theoretical amount of kaolin (less water) and is considered to be within the accuracy of the experiment. This result suggests that kaolin is unchanged, apart from dehydration.

The following statements can now be made, based on the analytical results:

1. The kaolin loses only water and does not react or enter into the combustion process (the equilibrium computer program suggested  $\text{Al}_2\text{O}_3$  and silanes might be produced).
2. With water and HCl present in the gaseous products, the CS is effectively maintained in an acid environment during vaporization.
3. Considerable amounts of HCl are generated and in association with water may serve to provide nucleating sites for the vaporized agent.



If the gases from a conventional CS mix are bubbled through water, the water becomes acidic, and if the ashes from this same pyrotechnic are placed in water, the water becomes slightly acidic. On the other hand, the gases from an MAA pyrotechnic bubbled through water give a slightly basic response and the ashes dissolved in water are highly basic.

Agent CS has been found to be very stable under acidic conditions and can be stored for months in highly acidic solutions without measurable degradation. We have stored samples in acidified water (pH 1.8) for one year without degradation; however, in a basic solution CS completely degrades in a matter of minutes. MAA on the other hand, is stable in basic solution but degrades under acidic conditions.

The acid-base nature of the pyrotechnic by-products are thus an important factor in deciding which agents can be disseminated using a particular fuel-oxidizer-coolant combination. More work needs to be done with various agent simulants and fuel-oxidizer combinations to firmly establish this conclusion.

#### B. Relationship of Composition, Thermochemistry, and Yield

Using the total collection method of analysis, we made a series of tests to study the effect of varying the CS level in the standard powdered mixture (nominal composition:  $\text{KClO}_3$ , 25 parts; NC, 3.2 parts; lactose, 19.8 parts; and kaolin, 11.5 parts; CS level variable). The prime goal of these tests was to obtain temperature and decomposition-product data for improving the computer program. Tests were performed in 2.3 inch diameter pyrotechnics containing approximately 235 grams of pyrotechnic mix.

Figure 23 shows the proportion of CS aerosolubilized and retained in the pyrotechnic ash after firing. It is interesting to note that optimum percentage aerosol yield is obtained at a loading level of 35% CS; as the loading increases, practically all the additional CS remains in the ash. Burning rate data for the composition are given in Fig. 24 and temperature data in Fig. 25.

It will be seen that a significant drop in burning rate occurs at the level of 35%. The flame temperature as measured by two embedded thermocouples, A and B in each pyrotechnic, is shown to be a smooth function of the CS diluent level. The significant change at a weight fraction of 35% suggests that an examination of the volumetric distribution of the pyrotechnic ingredients may confirm that high levels of CS form a system in which the CS is a continuous rather than a dispersed phase in the pyrotechnic body.

In another series of tests the kaolin-KClO<sub>3</sub> ratio was varied using standard amounts of CS, NC, and lactose (40% CS, 3.2% NC, 19.8% lactose, and 37% KClO<sub>3</sub>-kaolin). The data show similar trends in that the optimum yield of CS is obtained at a stoichiometry close to that of the standard formulation. The results of these tests are shown in Fig. 26.

In order to elucidate the role played by the coolant (kaolin) in the standard CS mix, several alternative materials were examined. Some of these compounds do not possess bound water. A summary of the data is presented in Table XI. The basic formulation used was: 40.6% CS, 19.4% lactose, 25.2% KClO<sub>3</sub>, 3.2% NC, and 11.6% clay.

All of the samples were prepared and pressed in the same manner. It is interesting to note that the clays all performed well--even a calcined clay which does not contain the bound water. Calcined diatomaceous earth appears to offer cooling and a fair yield, but the alkaline metal carbonates gave an extremely poor yield and, with the exception of NaHCO<sub>3</sub>, the temperatures were not exceedingly high. Further study is required to determine the function of the coolant, since it is obviously not a simple cooling process associated with the release of bound water.

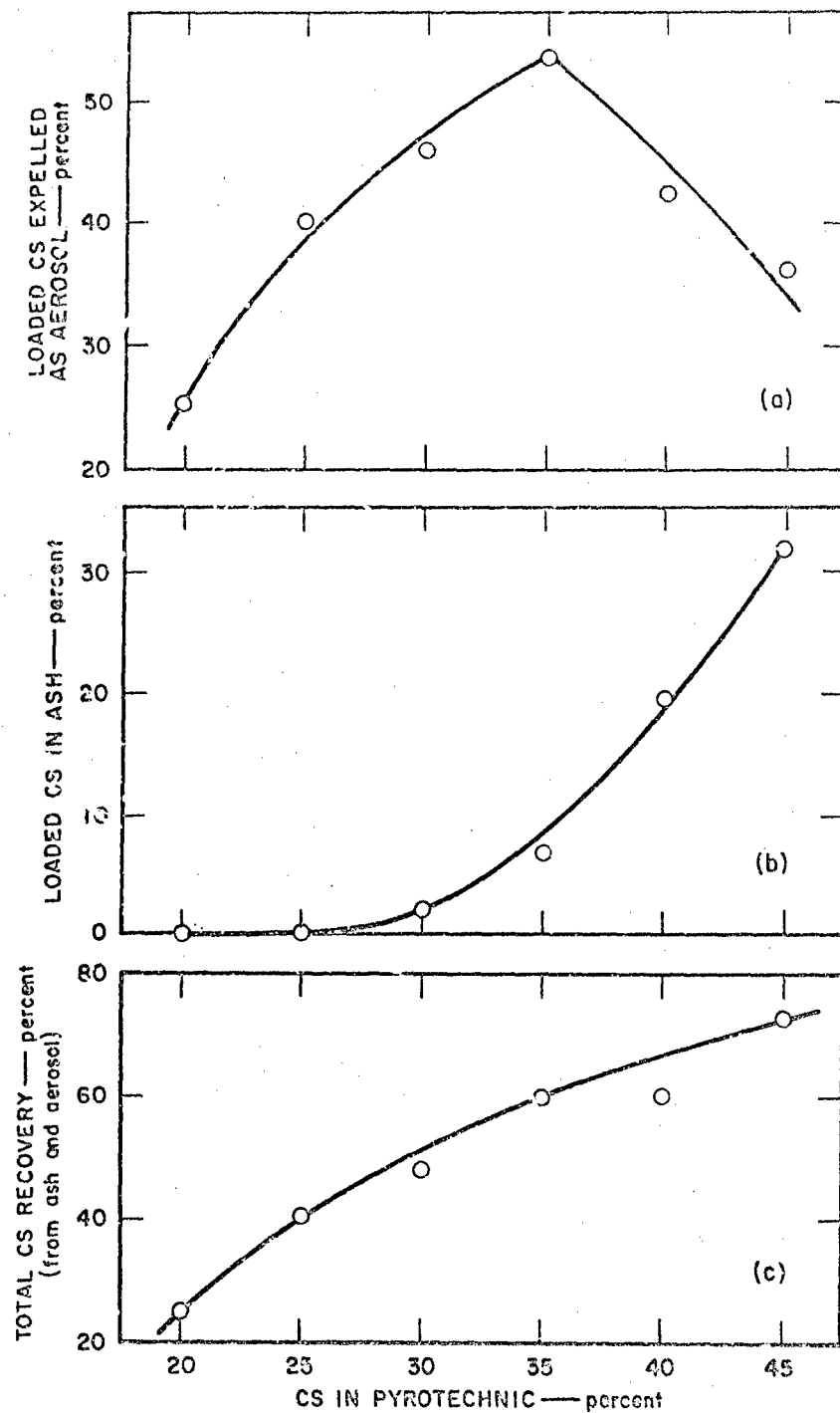


FIG. 23 INFLUENCE OF CS CONTENT ON:  
a) AEROSOL YIELD  
b) RESIDUE CS IN ASH  
c) TOTAL ANALYTICAL RECOVERY OF CS

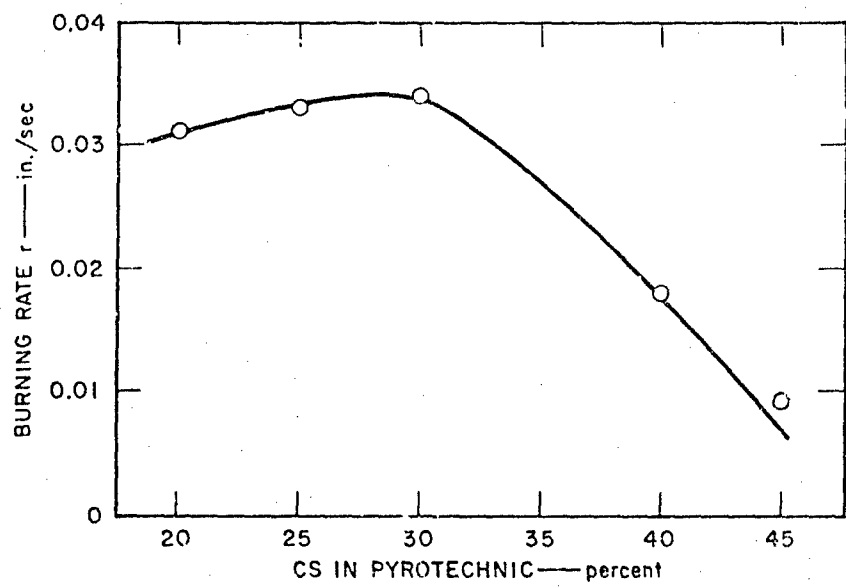


FIG. 24 RELATIONSHIP OF LINEAR BURNING RATE  
TO CS LEVEL

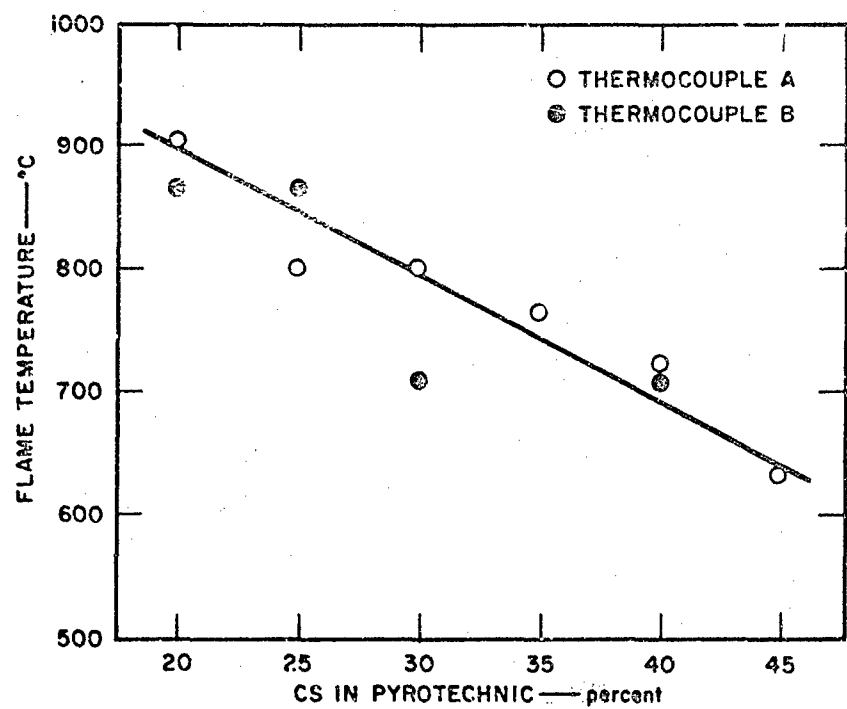
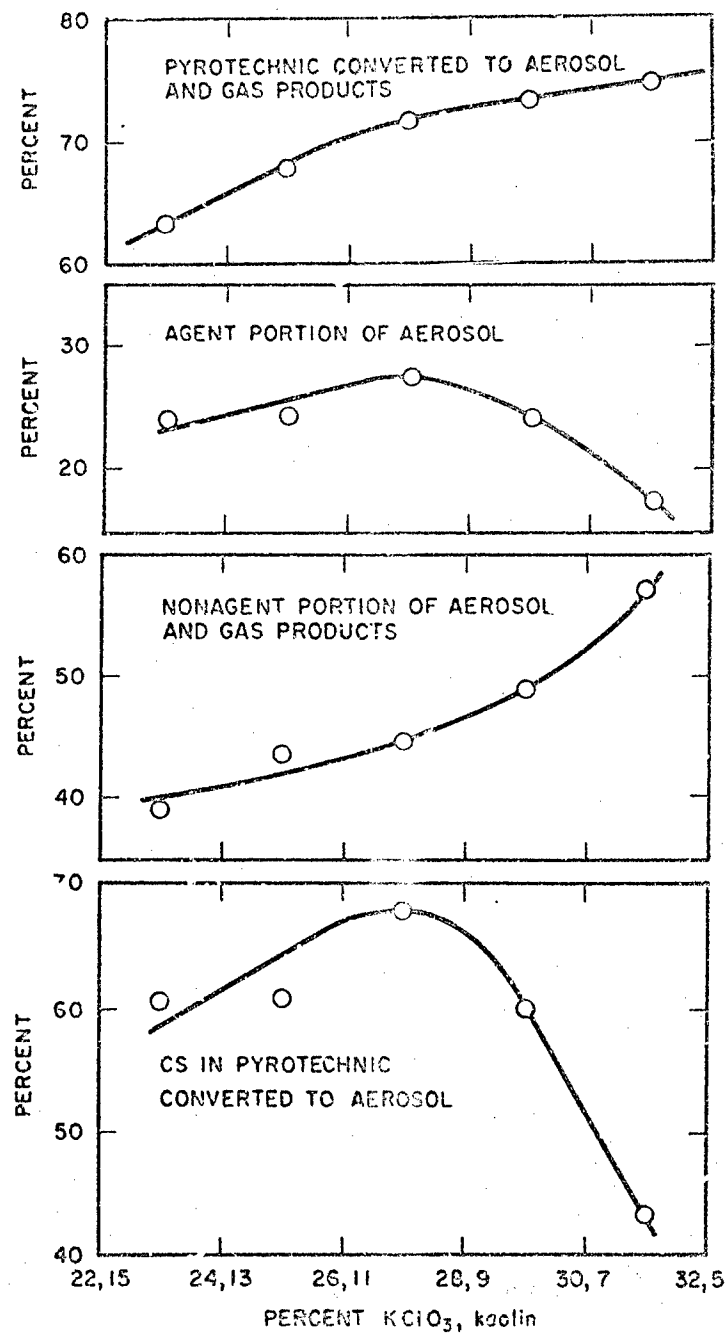


FIG. 25 INFLUENCE OF CS LEVEL ON MEASURED FLAME TEMPERATURE



TA-4800-726

FIG. 26 EFFECTS OF KClO<sub>3</sub> — KAOLIN RATIO

Table XI  
INFLUENCE OF COOLANTS ON AGENT YIELD

Clay	NaHCO <sub>3</sub>	MgCO <sub>3</sub>	CaCO <sub>3</sub>	D. E. *	Trans-link 37**	Maso.s Blend†	Cal Clay†	Pozzolan‡	White Tex**	Catalpa#	Kaolin, Calcined**	Control (Mil Spec Kaolin)
Pyrotechnic expelled (wt %)	74.1	70.4	70.4	68.7	67.9	69.2	70.0	69.2	70.0	67.1	66.3	
Pyrotechnic (wt %)	25.9	29.6	29.6	31.3	32.1	30.8	30.0	30.8	30.0	32.9	37.7	
Total residual (g)	57.0	63.0	66.0	75.0	74.0	69.0	67.0	74.0	68.0	76.0	79.0	
Burning rate (in./sec)	0.013	--	0.017	0.014	0.012	--	0.016	0.014	0.014	0.013	0.014	0.013
TC 1 Nozzle (°C)	500	340	465	440	505	--	447	425	447	337	--	485
TC 3 (°C)	770	700	740	725	725	--	675	725	735	707	672	705
TC 4 (°C)	815	--	770	725	720	682	682	732	742	670	780	705
CS expelled (%)	7.5	52.7	45.5	63.7	58.9	59.1	69.5	69.5	68.5	68.0	60.0	60.4
CS in residue (%)	0	5.68	4.19	3.12	7.59	6.16	3.44	3.49	1.94	11.7	7.3	0.8
Total CS recovery (%)	7.5	58.4	49.7	66.8	66.5	65.3	72.9	73.0	70.4	79.7	67.3	64.2

\*Diatomaceous earth.

\*\*Calcined kaolinitic clays, rubber grade, pH value 5.5 - 6.0.

‡Kaolinitic clays, cement grade.

†Finely divided alumina silicate, cement grade.

#Kaolinitic clay, rubber grade, pH value 7.0 - 7.5.

### C. Residence Time Experiments

An effort was made to isolate the important variables which affect the output of agent disseminated from a pyrotechnic. Initially, the obvious variables were assumed to be (1) processing techniques such as forming pressure, orifice size, and blending of ingredients and (2) ballistic parameters such as burning rate, temperature of burning, and pressure of burning. Another major variable is certain to be chemical composition.

It was noted in reviewing the data that the output seemed to be related to the action time (burning time) of the pyrotechnic as well as to the size. In order to check this observation, three pyrotechnics were made and burned which contained a nominal 240 grams of CS pyrotechnic mix with different burning surface areas.

The dwell time of agent in the flame zone and the char bed of the pyrotechnic can be equated to a residence time which is characteristic of the free volume in the canister and the flow rate of the combustion products. The residence time should be of importance in determining the extent of thermal pyrolysis undergone by the agent during the dissemination process. The critical nature of the residence time was demonstrated by measuring the agent output as the residence time was changed by an order of magnitude. Variations in residence time may be obtained in several ways:

1. By increasing the burn rate of the pyrotechnic mix.
2. By increasing the pyrotechnic density to better utilize the overall volume.
3. By increasing the burning surface area to decrease action time.
4. By increasing the size of the pyrotechnic.
5. By decreasing the free volume in the pyrotechnic.
6. By using a mixture which produces more gas to increase flow rate of gases.
7. By increasing the gas temperature (this results in increased gas volume).



All of the approaches for variation of residence time were reviewed, and an experiment was outlined to vary residence time using a constant formulation; this eliminated item 6, which would require a formulation change.

Although other methods were investigated, the most successful method of changing the residence time was by changing the free volume and the burning surface area simultaneously. This technique allowed an order or magnitude change in residence time to be obtained.

Using conventional concepts of residence time in a chemical reactor the residence time  $\tau$  is given by

$$\tau = - \frac{V_R}{\dot{V}_F}$$

where

$\tau$  = residence time

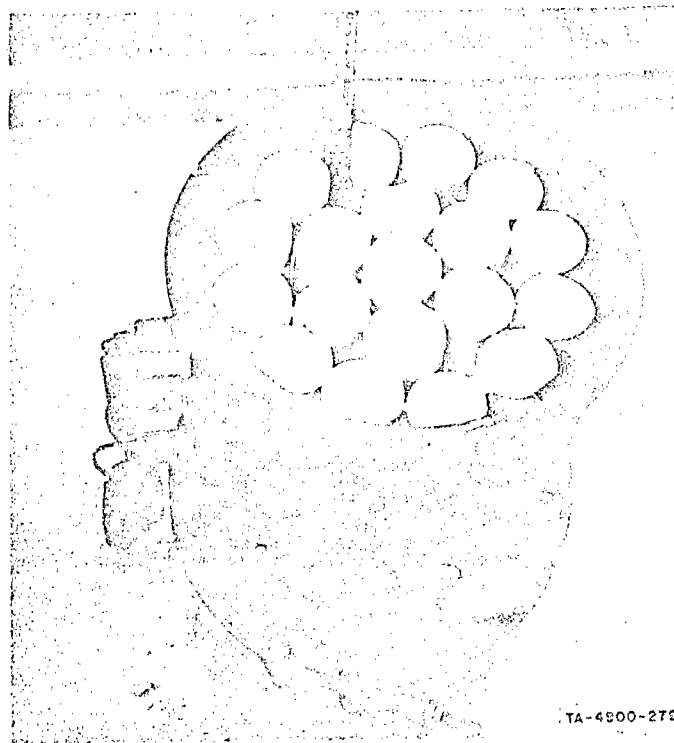
$V_R$  = volume of reactor (liters)

$\dot{V}_F$  = volume flow rate (liters/sec)

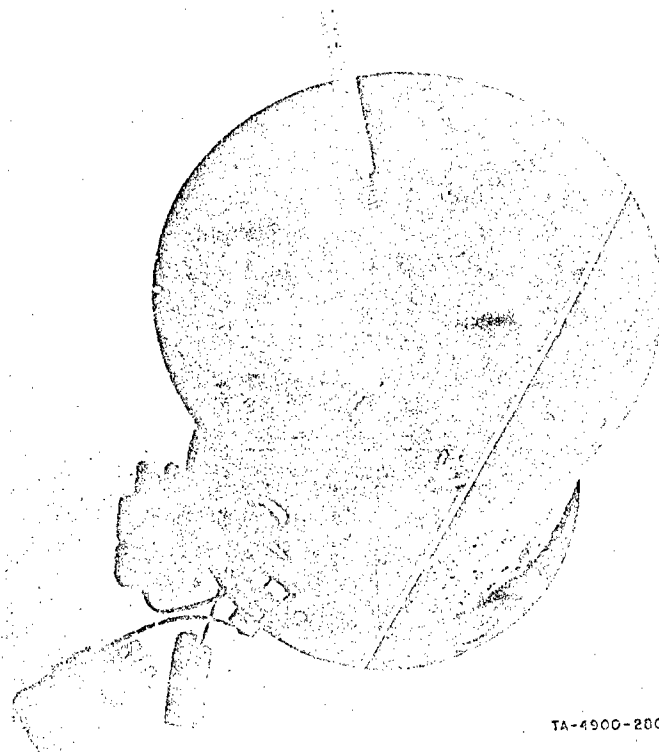
In order to apply this concept to a pyrotechnic, the simplifying approximations can be made that the combustion products remain at a uniform temperature after formation inside the device and that the volume of the ash residue does not seriously alter the flow velocity. In actual devices the free volume changes during burning; however, for comparative design purposes it is sufficient to compare the initial, final, or average residence times.

A larger pyrotechnic was designed for demonstration of residence time and for studies involving size as a parameter, since physical limitations of the 5.85 cm diameter would not allow the internal design flexibility required. The large pyrotechnic was 12.7 cm diameter x 17.8 cm long. The 12.7-cm-diameter unit was instrumented in a fashion similar to that of the 5.85-cm-diameter unit.

Figure 27 shows one test configuration of the large unit. The thermocouple outlets can be seen on the side of the pyrotechnic.



(a) BEFORE TEST



(b) AFTER TEST

FIG. 27 LARGE PYROTECHNIC DESIGNED  
FOR SHORT ACTION TIME

Pressure measurements were made through the end plate. The pyrotechnic was made in several configurations including a solid endburner and a perforated design. The configuration shown was made by pressing the free standing rods and then packing them into the unit. An ignition wire can be seen in the "before test" picture threaded through the rods of CS pyrotechnic mixture.

A larger receiver was used for collecting the agent and gases from the very large pyrotechnics (1800-3000 grams). This was found to be necessary for very short action time pyrotechnics because of the high rates of gas flow. The test arrangement for the 12.7-cm-diameter pyrotechnic is shown in Fig. 28.

For the size of pyrotechnic device under study, flow rates can be calculated from a knowledge of the gases produced. Inside the device there consist of noncondensable combustion products and CS at the combustion temperature. The standard CS formulation was used for these tests. CS output was collected by the previously described methods. Only the very large high-flow-rate units required special attention, and several tests were made before satisfactory recoveries were made.

Gas volume generated per gram of pyrotechnic was assumed to be constant since temperatures were not far different for any of the tests. Gas volume was based on measurements made during the material balance studies in which a value of 0.52 liters of gas/gram of pyrotechnic was determined. This value was obtained by measuring the total gas output and by correcting to a temperature of 600°C.

The free volume was calculated based on a density of 1.5 g/cc which was measured at a forming pressure of 10,000 psi. In order to obtain a final free volume, the ash was pulverized and the density measured using heptane as a fluid. Two ash density measurements were made for each sample with extremely good agreement between tests. A sample calculation of residence time follows:

$$\tau = \frac{V_R}{\dot{V}_F}$$

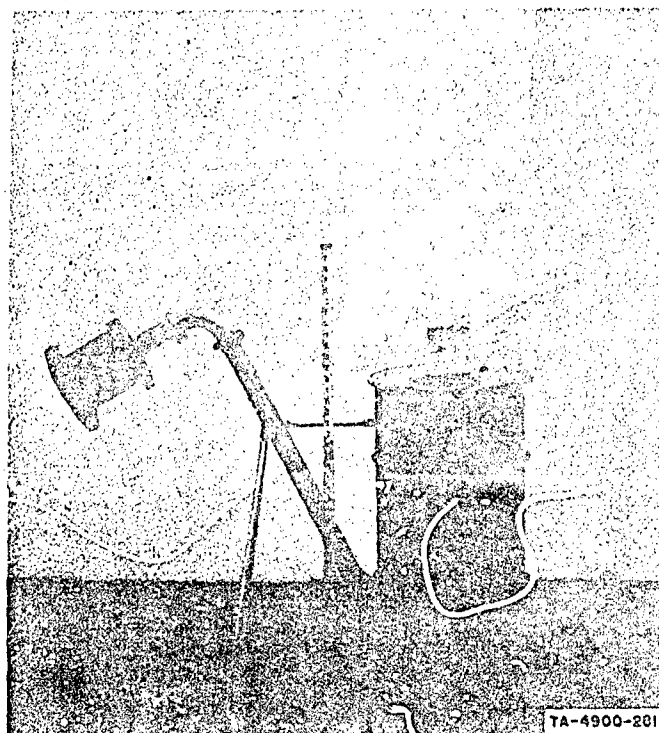


FIG. 28 COLLECTION APPARATUS  
FOR LARGE PYROTECHNICS

$$\dot{V}_F = \frac{\text{volume of gas generated (at combustion temperature)}}{\text{burn time of the pyrotechnic}}$$

Using data from the first pyrotechnic in Table XII, the volume of gas generated can be calculated to be 69.4 liters. Using the burning duration of 179 seconds, the volumetric flow rate is 0.4 liters/sec, giving an initial residence time of 0.42 seconds. After burning, the free volume changes to that of the canister less that of the ash. The final residence time is calculated using the same flow rates but a new free volume. The volume change is approximately constant for the small-scale pyrotechnic, and an average final volume is 0.262 liters. Thus, the final residence time is 0.66 seconds.

It was previously reported that the data were not adequate to correlate the relationship of residence time with output. The data were reviewed;

Table XII

## AGENT YIELD FROM

## A SERIES OF PYROTECHNIC DEVICES

Pyrotechnic weight (g)	Gas weight (g)	Residue weight (g)	CS output (g)	Gas volume (liters)	Action Time (sec)	Initial free volume $V_i$ (liters)	Final free volume $V_f$ (liters)	Initial Residence Time $T_i$ (sec)	Ave $T$	Final Residence Time $T_f$ (sec)	CS	
											Percent Aerosol Yield	Percent Recovered
223.3	133.45	89.85	51.6	69.4	179	0.166	0.262	0.42	0.54	0.66	57	--
244	156.27	87.73	48.5	81.2	176	0.153	0.262	0.33	0.45	0.57	49	66.5
244.3	150.6	93.7	45	78.3	135	0.153	0.262	0.26	0.36	0.45	45	64.5
266.5	169.2	97.3	55.7	88.0	147	0.138	0.262	0.23	0.34	0.44	51.2	64
242.8	154.6	88.2	47.0	80.39	240	0.153	0.262	0.46	0.62	0.78	47.5	63.0
234.9	141.5	93.4	45.4	73.5	218	0.158	0.262	0.47	0.63	0.78	47	70.5
261.0	164.0	97.0	69.4	85.2	58	0.147	0.262	0.1	0.14	0.178	65	73.2
282.0	195.6	86.4	72.0	101	77.4	0.127	0.262	0.09	0.15	0.21	63	69.6
233	140.9	92.1	59.0	73	52.0	0.160	0.262	0.08	0.14	0.189	62	72
1710	1268	442	580	660	45	0.85	1.734	0.045	0.068	0.092	83.5	85
13.8	5	7.82	2.61	2.6	58	0.015	0.022	0.3	0.4	0.5	18	--
210	154	54	51.3	80	9	0.184	0.262	0.02	0.025	0.03	72.2	75.4
2335	1718	617	603	1210	171	0.510	1.588	0.072	0.145	0.22	63.6	--

some discrepancies were found and additional data points were added. A least squares fit was obtained and plotted (Fig. 29). The correlation coefficient was found to be equal to  $-0.896$ . This value indicates that the probability of getting a correlation coefficient as good as has been obtained when none exists is less than  $0.001$ . This is considered to be acceptable evidence that a correlation has been established between residence time in the pyrotechnic and yield.

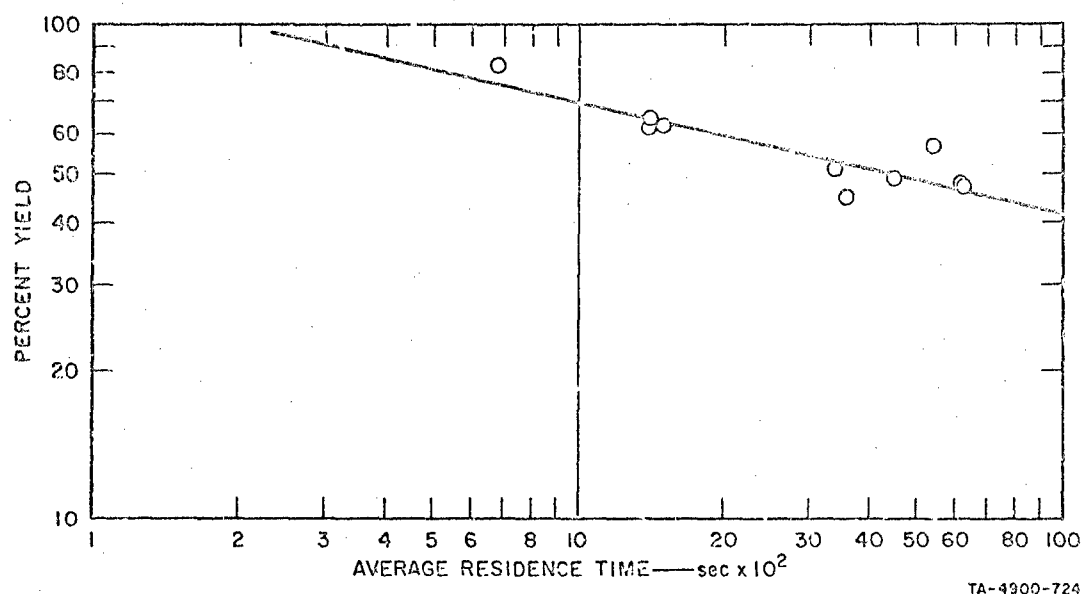


FIG. 29 PLOT OF % YIELD vs RESIDENCE TIME

Because of a difficulty in recovering agent and because of variances introduced by the different configurations required, it is felt that more data should be taken. Certainly an improved correlation could be obtained if a better model of residence time were formulated. However, the present model does demonstrate the potential importance of residence time in determining the dissemination efficiency of a pyrotechnic design.

#### D. Experimental Study of the Combustion Zone

There is considerable information in the open literature on the nature of the combustion zone at the surface of homogeneous and

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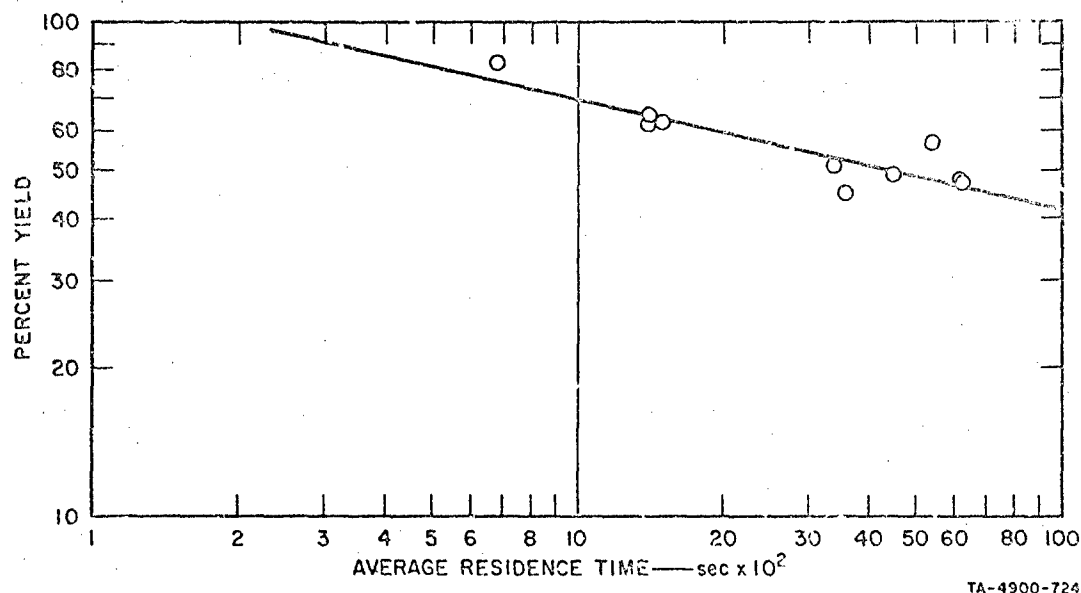


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There is considerable information in the open literature on the nature of the combustion zone at the surface of homogeneous and

heterogeneous solid rocket propellants. While the general nature of the combustion of a solid propellant is well understood, the discreet micro-ballistic phenomena of heterogeneous propellants or pyrotechnics have not been completely explained.

In our work it was decided to examine the temperature profile of the combustion zone in an attempt to define the thermal environment in which the agent must survive. Next, the pressure sensitivity of the burning rate was examined to ascertain if rocket propellant design concepts could be used in the study of pyrotechnics. Finally, a study of the physical and chemical characteristics was undertaken to provide data for the combustion modeling study.

#### 1. Thermocouple Measurements

Embedding of thermocouples in the pyrotechnics was done throughout the program. The thermocouples were installed through the side of the pyrotechnic using Conax fittings with a neoprene rubber seal. Couples were not placed in holes drilled into the pyrotechnic but were pressed directly into the mix between incremental pressings. Even though the thermocouples were positioned horizontally over the pressed increment, they sometimes shifted on further pressing, resulting in a damaged couple. This was not a common occurrence, and continuity and resistance were checked before each test. At first, glass beads were placed around the couples in some tests to protect them from the direct combustion environment, but no change in temperature readings was noted. Since the increased response time caused by the presence of the beads was a disadvantage, this practice was discontinued. The thermocouples which were used were 0.010-in.-diameter Chromel-Alumel from L and L Thermo-Engineering, precalibrated at three temperatures: 200, 400, and 600°C. The thermocouple calibrations are traceable to NBS standards (Test No. 175190-17). One order of thermocouples showed calibration errors of only 0.2°C, while the next order of couples showed calibration errors of 2°C at 200, 400, and 600°C. An ice bath was used for a reference junction. Chromel-Alumel wire was used throughout the system, which was calibrated daily using a null potentiometer. Output of the



tests was recorded continuously on a recording galvanometer (12 channel Visicorder) with approximately 1 in. of deflection/100°C.

During the combustion of a pyrotechnic, a quasi-steady temperature profile is established: a significant factor is the heat conduction from the primary combustion zone to the surface which preheats the pyrotechnic. In examining the temperature profile data, it will be seen that there is no sharp demarcation which defines a narrow primary reaction zone.

Typical temperature and pressure measurements for MAA pyrotechnics are shown in Figs. 30 and 31. The thermocouples are pressed into the pyrotechnic at evenly spaced intervals. Although the units were identical except for orifice size, the effect of this parameter is quite evident. One pyrotechnic unit operated at ambient pressure had an action time of 230 seconds while the other unit operated at  $2\frac{1}{2}$  atmospheres pressure had an action time of only 125 seconds. This is an

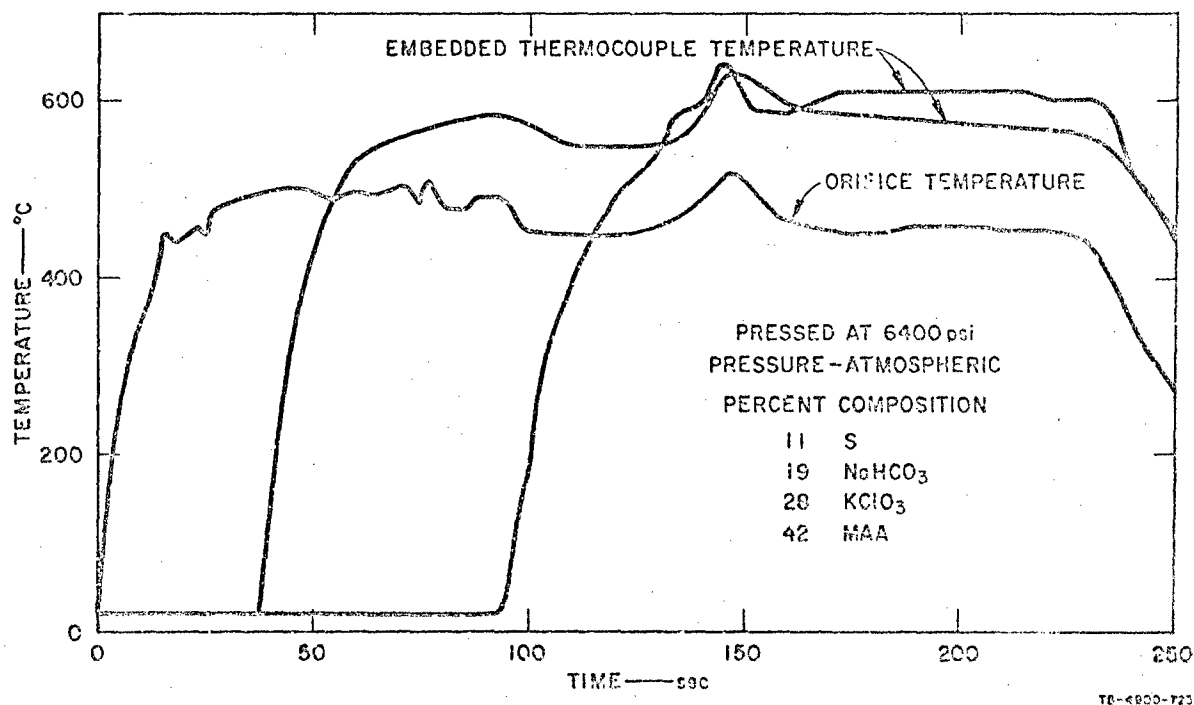


FIG. 30 TEMPERATURE MEASUREMENTS FOR A TYPICAL MAA PYROTECHNIC

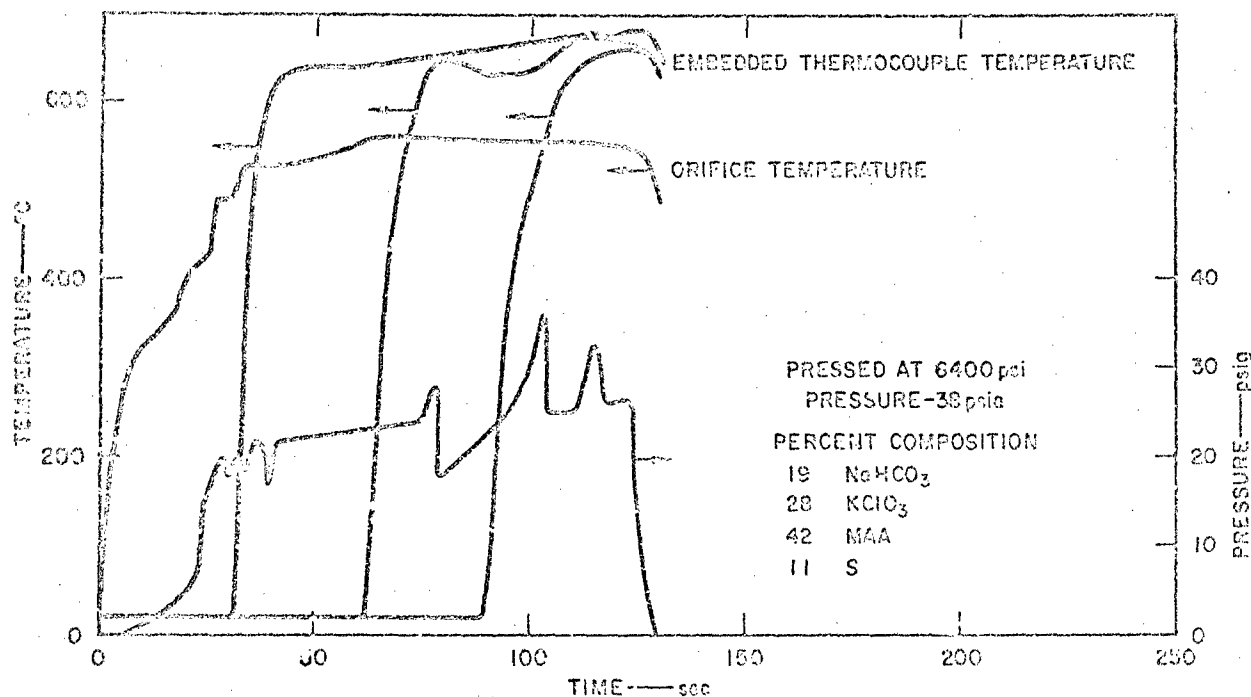


FIG. 31 TEMPERATURE AND PRESSURE MEASUREMENTS FOR A TYPICAL MAA PYROTECHNIC

indication of the gains in action time attainable through the use of higher pressures which give correspondingly higher burning rates. Formulation changes would be necessary to optimize high pressure operation, since temperatures in the pressurized unit were 50-75°C higher than those obtained in the low pressure unit.

It should be noted that the rate of temperature rise varies as the reaction zone progresses through the pyrotechnic mixture. This is an indication that the preheat zone grows progressively thicker as the char bed thickness constantly increases. It is probable therefore that the output or yield varies as a function of the thickness of the web of the pyrotechnic. Heat transfer in the solid phase, ahead of the reaction zone, contributes significantly to the burning rate through temperature changes in the solid pyrotechnic mixture. In addition, it can be hypothesized that agent yield is not constant during the full action time and that agent yield is continually degraded or upgraded depending on formulation as the pyrotechnic action time progresses.

Thermocouple measurements were also made on CS pyrotechnics; two typical records are shown in Figs. 32 and 33. In this case attempted operation at higher than ambient pressure led to chuffing (Fig. 33). Chuffing, which can be described as a series of extinctions and reignitions, is usually associated with intermittent heat transfer and thermal explosions in the solid phase. Time was not available for the exploration of possible remedial methods for suppressing the pressure surges. Other formulations may not suffer from this problem, especially if the fuel and oxidizer are homogeneous. A visual interpretation of this phenomenon is that the  $\text{KClO}_3$  spontaneously decomposes in layers which causes the alternately fuel-rich and oxidizer-rich surfaces to become exposed. Although it was impractical to determine the burning rates under high pressures in the pyrotechnics, the strand bomb measurements indicated that the burning was smooth in the larger volume of the bomb. No surges occurred, or if they did occur, they were masked on the pressure readout by low amplitude due to the large volume of the chamber.

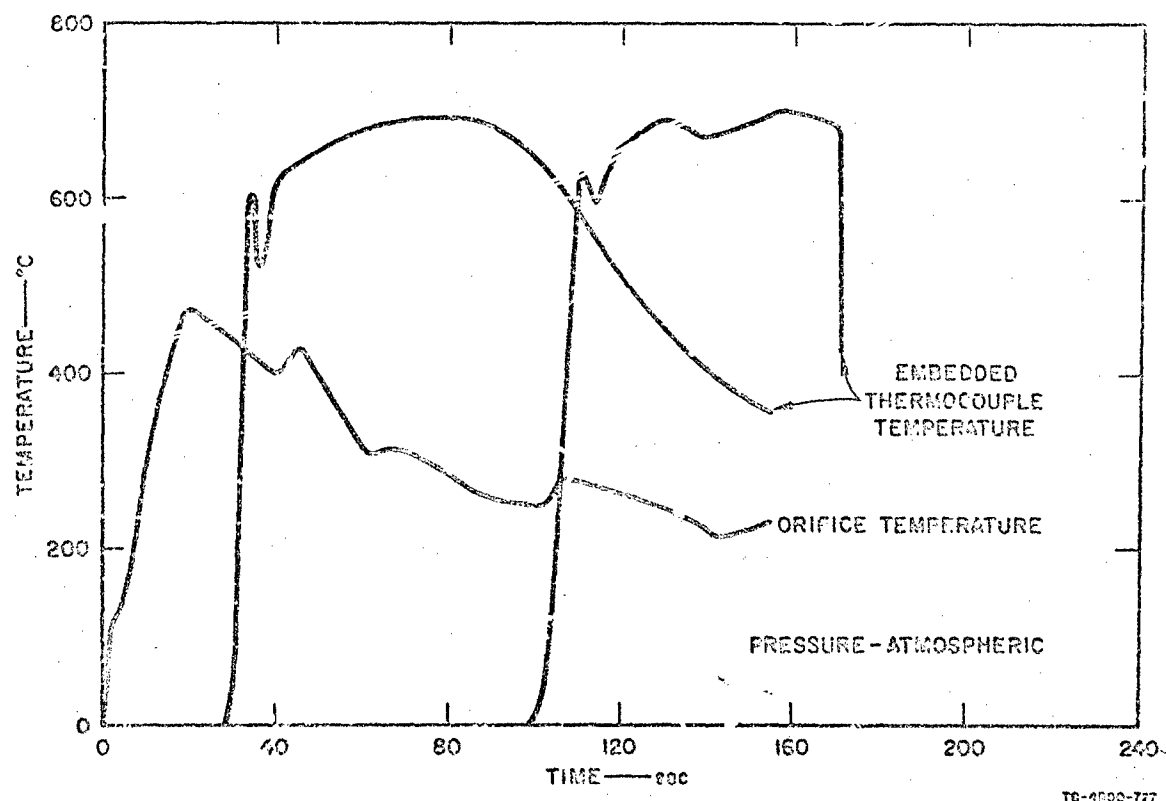


FIG. 22 TYPICAL CS PYROTECHNIC THERMOCOUPLE MEASUREMENTS

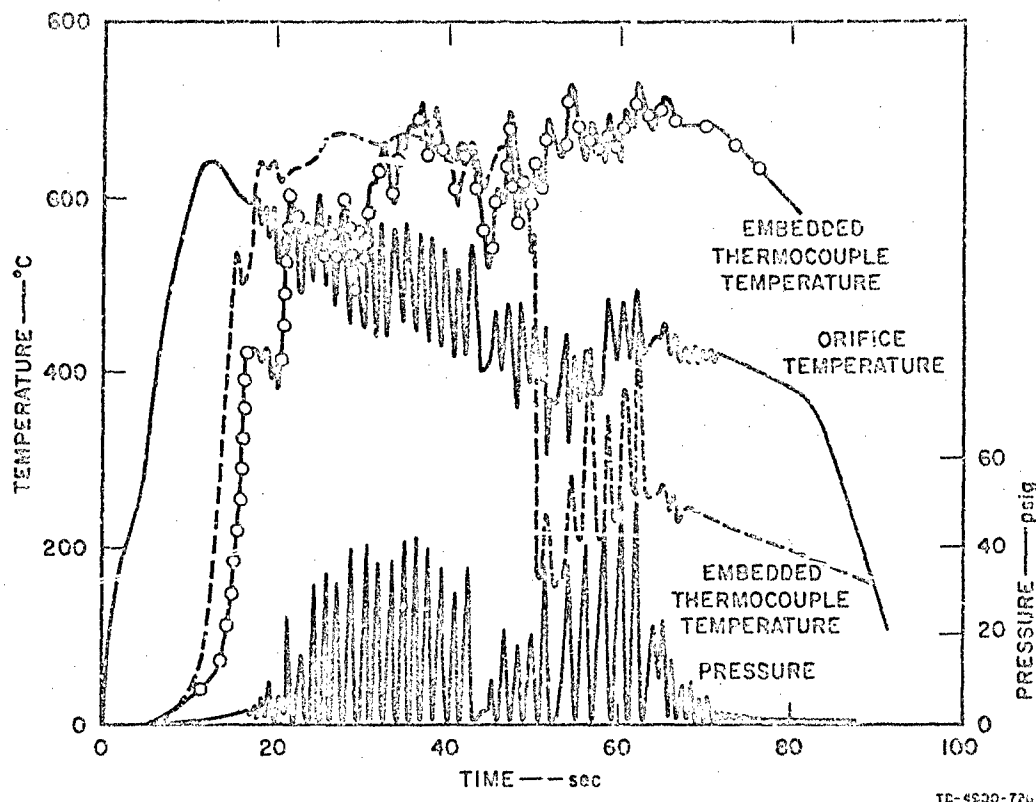


FIG. 33 TYPICAL CS PYROTECHNIC THERMOCOUPLE AND PRESSURE MEASUREMENTS

## 2. Photographic Studies of Burning Pyrotechnics

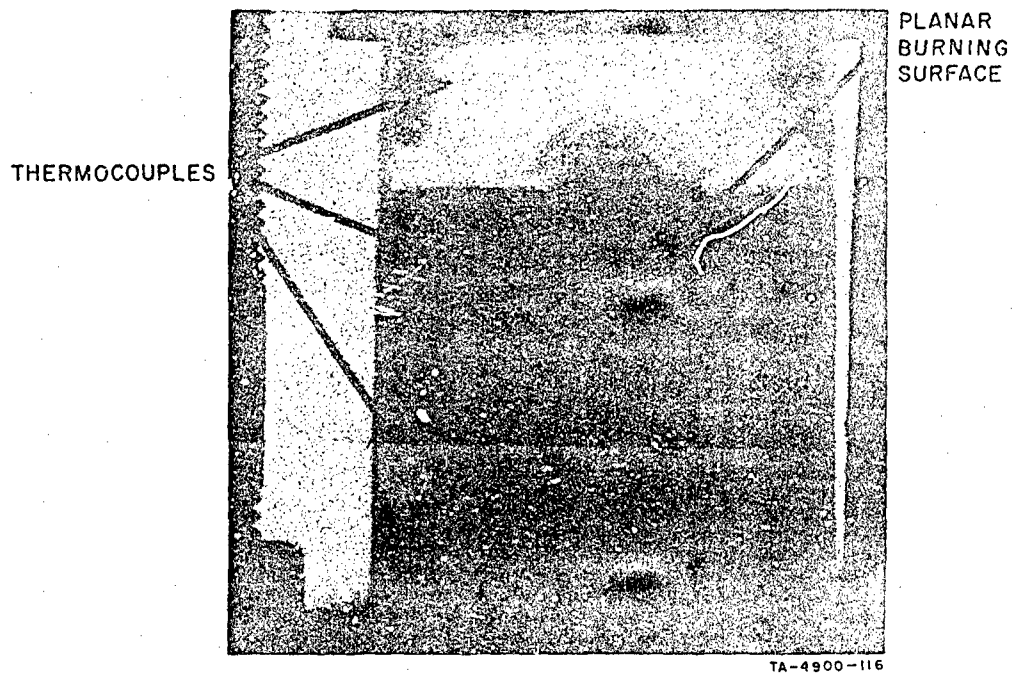
In an attempt to gain insight into the reaction processes occurring in the combustion front of the burning pyrotechnic, photographic studies were carried out using infrared film. The pyrotechnic was pressed into glass canisters for these studies. At the temperatures involved in the combustion of pyrotechnics, between 500-1000°C, approximately 97% of the radiation emitted is in the range 15,000 to 20,000 Å, while the Type 413 Polaroid film used in our studies has a usable wavelength range of 3,700 to 9,200 Å. Although this sensitivity range was not adequate to provide an outline of the flow characteristics of the hot gases in the device, it was adequate for identifying the path of the combustion wave through the body of the pyrotechnic.

From the photographs obtained, there is an indication that the burning surface is not homogeneous. It appears to consist of discrete particles

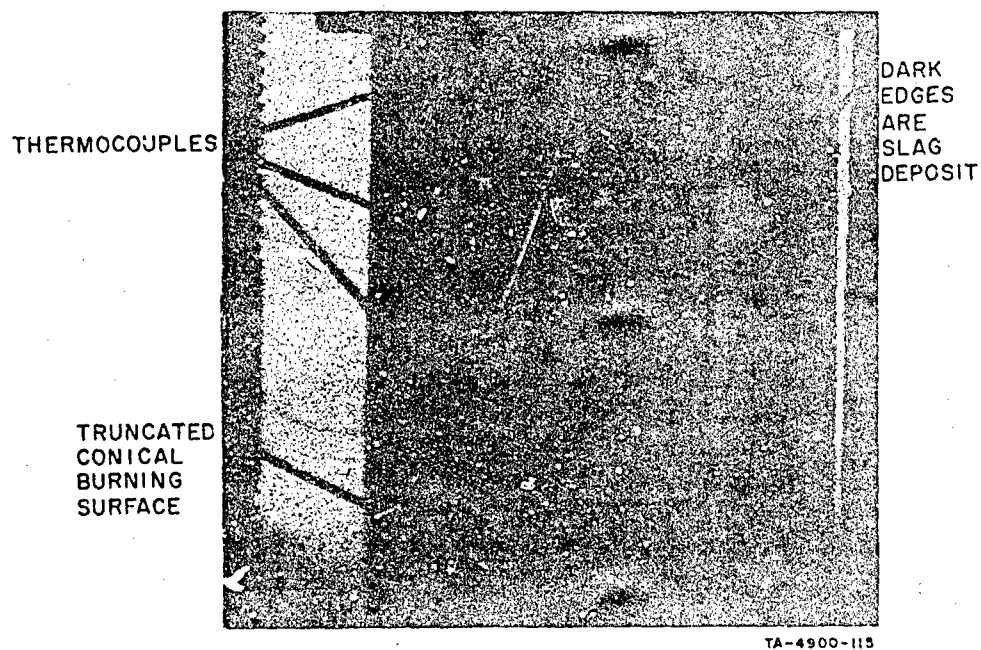
spontaneously decomposing with a release of energy which has sufficient local intensity to be detected by the Type 413 Polaroid film. Two compositions were studied: the first, Composition A, comprises 42% MAA, 26%  $\text{KClO}_3$ , 19%  $\text{NaHCO}_3$ , and 11% sulphur; while Composition B comprises 40.6% MAA, 29.1%  $\text{KClO}_3$ , 19.3% sugar, 7.9%  $\text{MgCO}_3$ , and 3.1% NC. Under similar exposure conditions, Composition B appears to have a thicker reaction zone than Composition A. Our estimate for the relative thicknesses are: 4 to 5 mm for B and approximately 1 mm for A.

As the reaction zone moves through the pyrotechnic, it leaves behind a thick char bed which is semi-liquid, i.e., it appears to be a solid bed with boiling liquid interspersed through the solid. This liquified portion appears to follow approximately 0.5-1 cm. behind the reaction zone. This would indicate that the efficiency of a pyrotechnic varies as a function of time from start to completion with the more efficient operation in terms of agent vaporization occurring during the latter stages of the functioning time.

In several of the previous tests using metal canisters, the thermocouple output became erratic because the thermocouples apparently melted during the last seconds of the run while the unit was operating at 500 to 600°C. As a result, it was decided that flash X-rays should be taken to determine whether the pyrotechnic was burning in an abnormal manner. A 5.85-cm-diameter pyrotechnic was tested with thermocouples pressed in place, and a series of 12 consecutive X-rays were taken during operation. The depth of the pyrotechnic material was 9.4 cm, providing approximately 120 seconds of burning. The X-rays indicate that the burning was uniform but that heat conduction down the metal wall of the pyrotechnic caused a conical burning surface, the cone having formed after 30 to 60 seconds of burning (see Fig. 34). In the design of large pyrotechnics, the heat of conduction down the wall must be considered, since formation of a cone can continuously increase the burning surface and can cause a pressure failure.



(a) SURFACE PROFILE AT START OF BURNING



(b) SURFACE PROFILE AT END OF BURNING

FIG. 34 SELECTED X-RAY PHOTOGRAPHS OF PYROTECHNIC BURNING DURING OPERATION

### 8. Tests with CRDL Furnished Pyrotechnics

A series of small CS pyrotechnic canisters (1x1 CS LI-B) were received from Edgewood Arsenal for testing. These units contained approximately 15 grams of CS pyrotechnic mix. The material was analyzed and found to contain 34.8% CS. The mixture was slurried and dried to form small granules of varying size which were pressed into canisters with outside dimensions of 2.54 cm diameter x 3.0 cm long. Two tests with these units delivered 73 and 78% of the CS which they contained. The same material was then formed at a pressure of 6400 psi into larger service-grenade-size canisters. The finished pyrotechnics each contained 240 grams of mixture. It was surprising to find that yields obtained from these units fell between 65.7 and 67.5%, well below the above values.

The small units burned out in  $10.2 \pm 0.8$  seconds, and based on the web thickness the calculated burning rate was 0.102 cm/sec (0.04 in./sec), or double the rate of previous endburners which were prepared without using a slurry process technique. However, when the same material was pressed at 6400 psi in the service-grenade-size units, the burning rate was measured to be only 0.02 in./sec. This is an indication that the burning surface inside the Edgewood Arsenal canisters includes flame front penetration into the interstices of the granules.

Very granular pyrotechnic was found in a sectioned 1x1 CS LI-B unit (see Fig. 35). The measured low bulk density of 1.05-1.08 g/cc is indicative of the lack of compaction. These porous granular pyrotechnic compositions permit very short action times but suffer from certain disadvantages. Burning times and burning pressures will vary, depending on granulation density and packing. This is not a serious problem with the small units, but in larger units the variation in pressing density, porosity, granulation, and burning surface area make the system of granular packing very difficult to use. Loosely packed granules would probably break up in units which had undergone severe vibration. This problem would be amplified accordingly for units of larger size. Difficulties would also be encountered when these units are operated at higher pressures, since the hot gases would probably break the entire particle surfaces, causing a pressure failure.

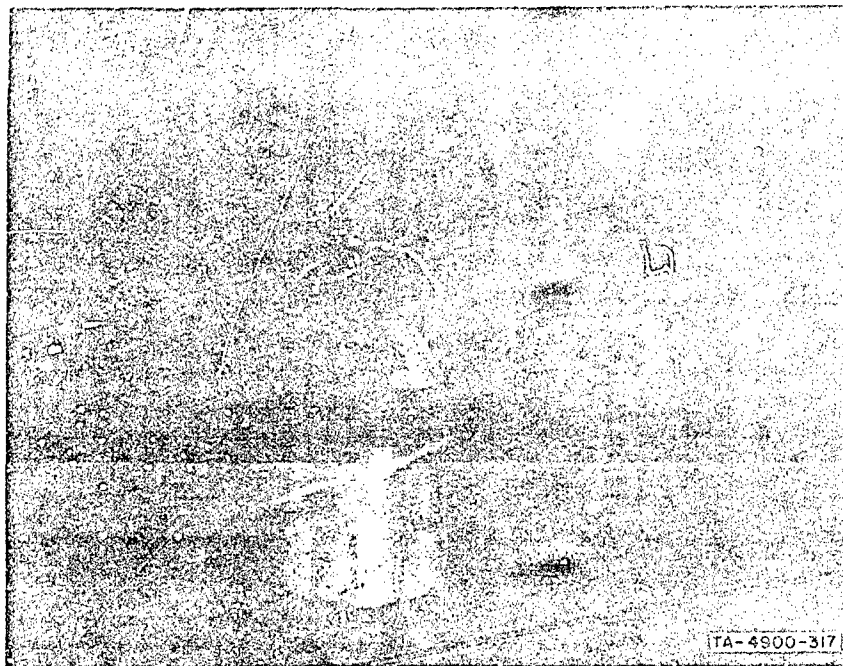


FIG. 35 1X1 CS LI-B CRDL PYROTECHNIC WITH  
PYROTECHNIC CHARGE REMOVED

It is interesting to note that the 34.8% CS loading used by CRDL is close to the optimum loading predicted in our studies. Since the CRDL used a different pyrotechnic formulation, the yield data cannot be directly compared to the data obtained in our residence time studies, but the short residence times of the CRDL pyrotechnic would be expected to give high yields.

A test was made to determine if yields could be attained on the order of the 73-78% measured in the (1x1 CS LI-B) small pyrotechnics in a service-grenade-size unit with the 35% CS mixture. A pellet press was used to make 0.375-in.-thick x 0.750-in.-diameter pellets. These were pressed to between 6400-10,000 psi and packed randomly into the canister. Results of this test are given in Table XIII. Although the yield from this test was not as high as that measured from the 1x1 CS LI-B units, it is comparable. If the pelletizing is done while the slurry still contains a controlled amount of solvent, the resulting dried pellet will be hard and durable and the burning time



will be quite accurately predictable. The total burning time of the pyrotechnic should also be controllable. In the original tests large mesh screens were fitted inside the outlet orifice to prevent the pellets from being blown from the canister by aerodynamic forces. Further work with pelletized pyrotechnic materials was planned but not completed because of the termination of the program.

Table XIII

SUMMARY OF DATA FROM PELLETIZED PYROTECHNIC TEST

<u>Parameters</u>	<u>Values</u>
Orifice diameter (in.)	0.375
Net weight of pellets (g)	210.0
Weight of gas (g)	154.0
Weight of residue (g)	54.0
Burning time (sec)	9.0
Peak-to-peak pressure oscillation (psig)	2-30
Temperature (2 embedded thermocouples)	745-745
Burning rate (in./sec.)	0.0153
Weight of CS expelled (g)	51.3
CS in Residue (%)	3.2
CS expelled (%)	70.0
Total CS accounted for (%)	73.2

E. Computer Studies

The importance of a computer program designed to evaluate pyrotechnic ingredients has been realized by other investigators in the field of dissemination. Programs have been developed for use on flares, heat-producing pyrotechnics, explosives, and rocket propellants. These programs have been successfully used to optimize formulations and to evaluate new additives for their effect on performance. No suitable programs are available for dissemination studies because true equilibrium conditions do not exist in a disseminating device.

Atlantic Research Corporation has performed many calculations.<sup>10</sup> Their calculational procedure was based on an assumed two-step process: combustion of the pyrotechnic followed by evaporation of the agent to provide an aerosol. However, the predicted temperatures and exhaust products did not correspond very well to the available experimental data. To improve the analysis, account must be taken of the significant portion of agent which is destroyed during the deflagration of a pyrotechnic, and which therefore must contribute to the total heat release. In an attempt to do this, our computer program was designed to treat a specified amount of agent as a part of the fuel. Since the computer program is necessarily based on equilibrium reactions, the amount of CS and other materials which react, as opposed to those which merely behave as diluents, must be determined. In an attempt to duplicate the analytical results several calculations were performed.

A computer format which treated 10.9% CS out of the original 40.6% as fuel was used to duplicate a typical test. The reaction temperature was fixed at 650°C and the pressure at one atmosphere. Table XIV lists significant computed equilibrium decomposition products expressed in moles/100 g of reactants. The calculation was repeated allowing the reaction (flame) temperature to seek its own desired equilibrium value. The calculated temperature was 709°C with a  $\Delta H = -12.58$  kcal/100 g of mix. This heat difference was then equated to the heat of vaporization of the fraction of the CS which was converted to aerosol. A  $C_p$  of 0.255 cal/g was assumed for CS with a heat of vaporization of 136 cal/g. The CS and vapor equilibrium temperature calculated using the above  $\Delta H$  was then 480°C (assuming no heat losses). The measured orifice temperature for a large CS pyrotechnic with minimal heat losses was 462°C, in good agreement with the calculated value.

The mole fractions in Table XIV did not agree with experimental results, since no silanes were predicted and the kaolin passed through the pyrotechnic unchanged. Accordingly, the mole fractions were modified to give the results shown in Table XV. This table compares the experimentally corrected results from the computer to those obtained experimentally. When reviewing the data it must be kept in mind that

the yield of CS was fixed before the calculation was made and that the purpose of the calculation was to compare solid and gaseous fractions and the behavior of the other constituents with measured results. Unfortunately, the computer program does not predict the carbon-containing compounds which were found experimentally, other than those of oxidized species. The effective use of the computer to predict equilibrium conditions is therefore limited by the available data on the products being generated.

Table XIV  
COMPUTER-PREDICTED DECOMPOSITION PRODUCTS

<u>Component</u>	<u>Gas evolution from pyrotechnic (Moles/100 g)</u>	<u>Gas composition after removal of water and HCl (wt %)</u>
CH <sub>4</sub>	5.5 x 10 <sup>-2</sup>	2.2
CO	7.5 x 10 <sup>-1</sup>	30.3
CO <sub>2</sub>	6.4 x 10 <sup>-1</sup>	25.9
HCl	1.1 x 10 <sup>-2</sup>	
SiH <sub>2</sub> Cl <sub>2</sub>	1.1 x 10 <sup>-3</sup>	1.4
SiHCl <sub>3</sub>	2.8 x 10 <sup>-3</sup>	0.6
H <sub>2</sub>	8 x 10 <sup>-1</sup>	32.5
H <sub>2</sub> O	3.4 x 10 <sup>-1</sup>	
N <sub>2</sub>	7.9 x 10 <sup>-2</sup>	3.2
SiO	9.5 x 10 <sup>-2</sup>	3.9
<u>Production of Solid Residue</u>		
Al <sub>2</sub> O <sub>3</sub>	6.73 x 10 <sup>-2</sup>	21.2
KCl	3.10 <sup>-1</sup>	71.2
C	2.0 x 10 <sup>-1</sup>	<u>7.6</u>
		100.0

Table XV

## COMPARISON OF EXPERIMENTAL AND COMPUTED PYROTECHNIC OUTPUT

	<u>Measured (wt %)</u>	<u>Calculated (wt %)</u>
<u>Residue Composition*</u>		
CS	25	25
KCl	35	44
KClO <sub>3</sub>	11	0
C	5	4.6
Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	<u>24</u>	<u>25.6</u>
	100	100.0
<u>Gas Composition</u>		
H <sub>2</sub> O	21.6	6.95
H <sub>2</sub>	0.02	1.64
N <sub>2</sub>	0.2	2.21
CO	14.2	21.08
CO <sub>2</sub>	21.8	28.35
CHCl <sub>3</sub>	0.3	0
C <sub>2</sub> H <sub>2</sub> (CN) <sub>2</sub>	0.6	0
C <sub>3</sub> F <sub>3</sub> Cl	0.07	0
HCl	3.20	2.42
CS	38.00	37.3
CH <sub>4</sub>	<u>0</u>	<u>0.95</u>
	99.99	100.00

\* The measured residue mass fraction was 0.4 and the calculated one was 0.36.

To perform a reasonable calculation, our approach assumes that the amount of agent destroyed is known, and further, from experimental results, that the agent destroyed is oxidized in an equilibrium manner. It is known that this second condition does not exist; in the case of CS, the agent actually is partially fragmented into cyanogen, chlorobenzene, and other components, and a portion is converted to a hydrocarbon char as shown by analysis of the ash.

An analysis was run on the pyrotechnic ash to determine if the Kaolin was converted to the chlorosilanes and  $\text{Al}_2\text{O}_3$ . The ash of a pyrotechnic was washed with water to remove KCl and the ash fired at  $850^\circ\text{C}$  to drive off volatiles. Kaolin was found to survive the combustion without change except for loss of water. No silanes were formed as would be suspected. Since the silanes did not form there was a shift toward the generation of hydrochloric acid. Generation of hydrochloric acid has been verified in concentrations which are far greater than those predicted by the computer program.

Since the computer program requires an input of the amount of agent burned, its greatest value lies in the prediction of possible unknown equilibrium compounds. However, it is possible to use the computer to predict output as a function of agent burned. After one or two points on the generated curve had been verified, the curve could be used with some credence. Further work is required to develop a program which would be truly useful. A summary of the thermal data which was used in the program is included in table XVI.

Table XVI

## INPUT INFORMATION TO COMPUTER PROGRAM

Chemical Heats of Formation

<u>Component</u>	<u><math>\Delta H_f</math> (kcal/mole)</u>
Potassium Chlorate, $\text{KClO}_3$	-93.50
Lactose	-505.2
Kaolin	-944
Nitrocellulose	-170.2
CS	+50.0
Sodium bicarbonate, $\text{NaHCO}_3$	-226.5
Sulphur, S	0.0

Physical Properties

$$\rho = 1.04 \text{ g/cc}$$

$$\text{BP} = 311.5^\circ\text{C}$$

$$\text{Vapor Pressure } \log_{10} P = \frac{-5933.7877}{T} + 11.81265 \log_{10} T + 45.644$$

$$\text{CS (solid) Specific Heat} = .255 \text{ cal/gm}$$

$$\text{Heat of vaporization} = 25,600 \text{ cal/mol}$$

## V CONCLUSIONS

An initial literature survey showed that many important phenomena had never been investigated in previous studies on pyrotechnics and model compounds, including the temperature profile through the combustion wave, the effects of operation at pressures other than ambient, and the effects of both chemical formulation and physical processing parameters on the output efficiency of pyrotechnics.

The principal experiments which were performed during the current investigation included adiabatic self-heating (ASH) measurements, differential thermal analysis (DTA) measurements, burning rate measurements as a function of pressure, temperature profile measurements in the combustion zone, and agent yield measurements utilizing a total recovery technique. A concurrent effort was made to develop a useful computer program which could predict the effects of formulation changes.

The ASH experiments defined the activation energy of a typical pyrotechnic and of binary mixtures of its ingredients and showed that a burning-rate derived activation energy is necessarily unreliable because of its dependence on the physical process of heat transfer. The DTA measurements defined the endotherms and exotherms to be expected as a function of temperature and were demonstrated to be a useful tool for screening out experimental mixes which have an exotherm at a dangerously low temperature. Burning rate studies indicated that pyrotechnics have a burning rate law which resembles that of solid propellants. The relationship obtained is not heavily dependent upon forming pressure, but at forming pressures below 2000 psi the burning rates under pressure were no longer reproducible or controllable. The data obtained provides a method for the design of pyrotechnics to operate at any chosen pressure.

Temperature profile measurements indicated that there is a significant preheat zone ahead of the combustion wave and that the char bed remaining after passage of the wave can significantly influence agent decomposition. Thermal conductivities of various pyrotechnic ingredients

have been determined and vapor pressure measurements have been made for MAA.

In order to obtain an accurate measurement of agent yield a total washdown of the chamber with subsequent recovery of all agent was employed. In addition to supplying a reliable sample this technique leads to safer operation since if all the agent is recovered, it may be properly decontaminated and disposed of instead of being collected on filters or being dumped into the atmosphere.

MAA is commonly used as a simulant for real agents such as CS because of its convenience and safety. For this reason MAA was extensively employed during the current investigation. It was found that although MAA pyrotechnics are useful for testing equipment for later use with agent-containing pyrotechnics they are of limited value for drawing any real conclusions concerning the use of agents in pyrotechnics unless the agents are of a similar chemical nature to MAA. Preliminary results show that the pyrotechnic formulation must be carefully tailored to match the acidic or basic nature of the agent if effective dissemination is to be achieved.

A complete material balance on the MAA pyrotechnic was only partially successful because of the complexity of, and the amount of ash remaining after firing. In addition, the size, action time, and pressure are all variables which are very significant contributors to the amounts of ash and its composition. The normal yield obtained was approximately seventy-five percent. Many of the combustion products have been determined and an approximate evaluation of the ash constituents has been made.

The search for a suitable burning rate catalyst for these pyrotechnic compositions was unsuccessful. A method of slightly increasing the burning rate was found through the addition of 5% of aluminum needles. The gain is not considered to be worthwhile since the needles are a diluent and do not react--their burning rate contribution is simply a method of increasing heat flow ahead of the combustion zone.

A correlation has been made of dissemination efficiency as a function of agent residence time in the pyrotechnic. This relationship indicates



that pyrotechnics should be designed to function as rapidly as possible, as one would expect. Since we were unsuccessful in increasing the burning rates by catalyst addition, it appears that the only way to decrease action time is by increasing burning surface area. If this technique is carried to the ultimate, a simple loose powder is the result. However, burning rates of loose powders are uncontrollable and much of the pyrotechnic mix is carried through the orifice to burn outside the pyrotechnic. Thus, it is necessary to reach some compromise between degree of subdivision or porosity and burning times.

Pyrotechnics of up to 3000 grams were made and tested. There were no signs of a runaway reaction and it would appear that there is no limit to the size of a pyrotechnic which can be built to function satisfactorily if the design prevents severe buildup of heat ahead of the combustion zone. The larger the unit tested, the more effective it appeared. In terms of loading density (grams of agent disseminated/cc of pyrotechnic) the larger the pyrotechnic, the more effective it is. The action time of large pyrotechnics is controllable over a wide range. If a pelletized pyrotechnic mixture is used and the pellets are simply packed, the burning time will be a constant regardless of the size of the pyrotechnic provided ignition is complete.

A series of tests with various kaolin-type clays indicated that the role of the clay is not simply as a coolant since calcined kaolin worked as well as mil spec kaolin, while  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{NaHCO}_3$  seriously degraded the agent output with  $\text{NaHCO}_3$  having the lowest yield of all. The temperature measurements indicate that  $\text{NaHCO}_3$  produced a significantly higher flame temperature than other coolants. This is probably due to interactions of by-products of  $\text{NaHCO}_3$  with agent and agent by-products.

Areas which are worthy of more research include physical and chemical methods of burning rate stimulation. The chances of finding a chemical technique of multiplying the burning rate by at least an order of magnitude are quite small because of the low temperatures involved and the restrictions imposed on possible reactions because of the presence of agent. A cast system instead of a pressed pyrotechnic

system would be expected to be more adaptable to burning rate catalysis. With present technology it appears that the most promising avenue to more rapid pyrotechnic dissemination is through design modification--as compared to formulation modification.

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## GLOSSARY

$A$	frequency factor in Arrhenius representation of kinetics
$A_b$	burning surface area of pyrotechnic
$A_t$	orifice of nozzle throat area
$c$	coefficient of burning rate law, $r = cp^n$
$c^*$	characteristic velocity of orifice or nozzle efflux
$D_o$	volume-to-surface area mean particle diameter
$E_a$	activation energy
$g$	acceleration of gravity
$k$	chemical reaction rate; specific heat ratio
$K$	chemical conductivity
$m$	slope of activation energy plot
$n$	exponent of burning rate law, $r = cp^n$
$p$	pressure
$r$	burning rate
$R$	gas constant
$T$	temperature
$T_a$	ambient temperature deep in the pyrotechnic
$T_f$	flame temperature
$V$	volume; voltage
$\dot{w}$	weight flow rate

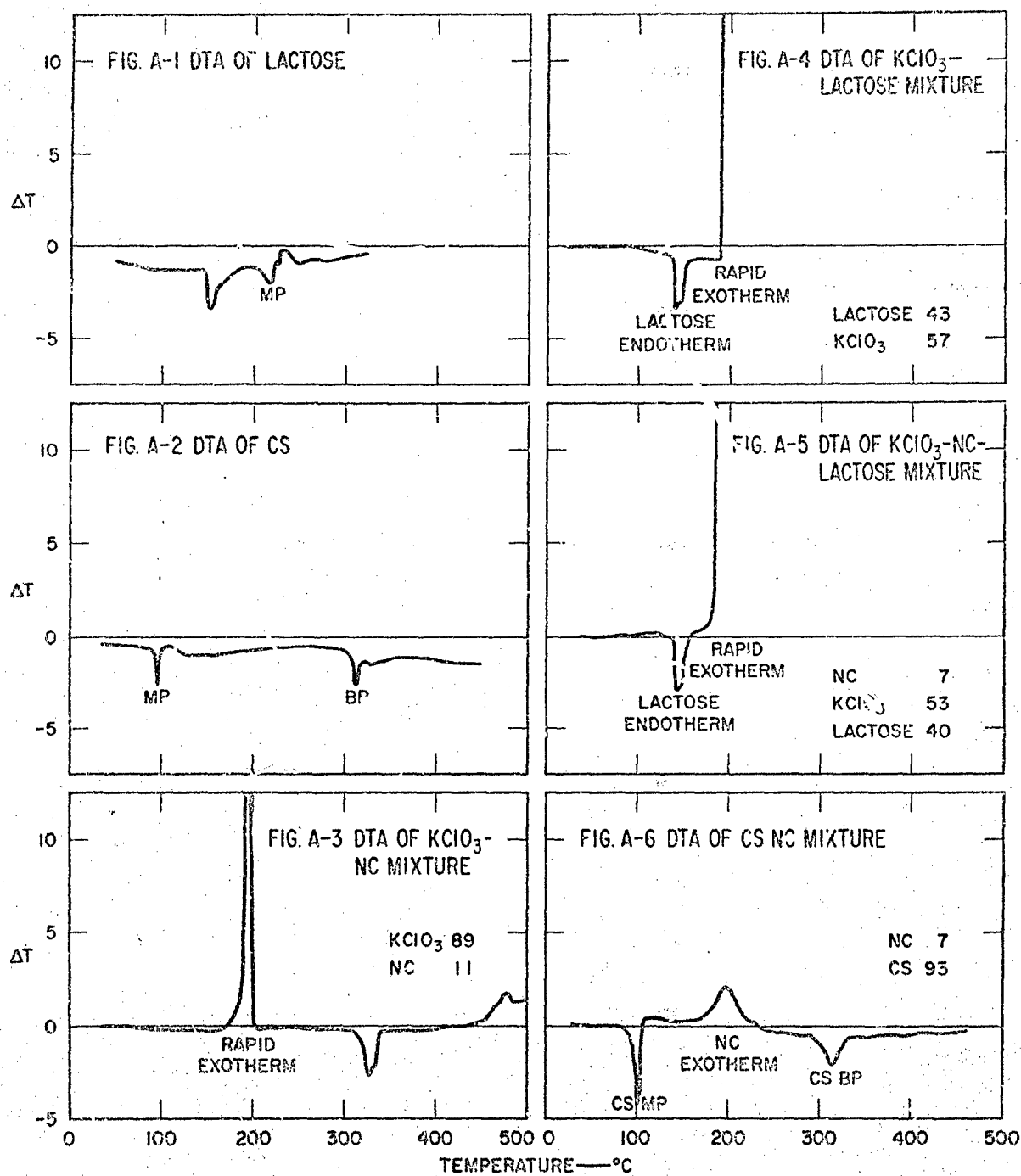
### Greek Symbols

$\Delta H_f$	heat of chemical formation
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$\Delta H_s$  heat of sublimation  
 $\Delta H_v$  heat of vaporization  
 $\rho$  density  
 $\tau$  residence time

## APPENDIX

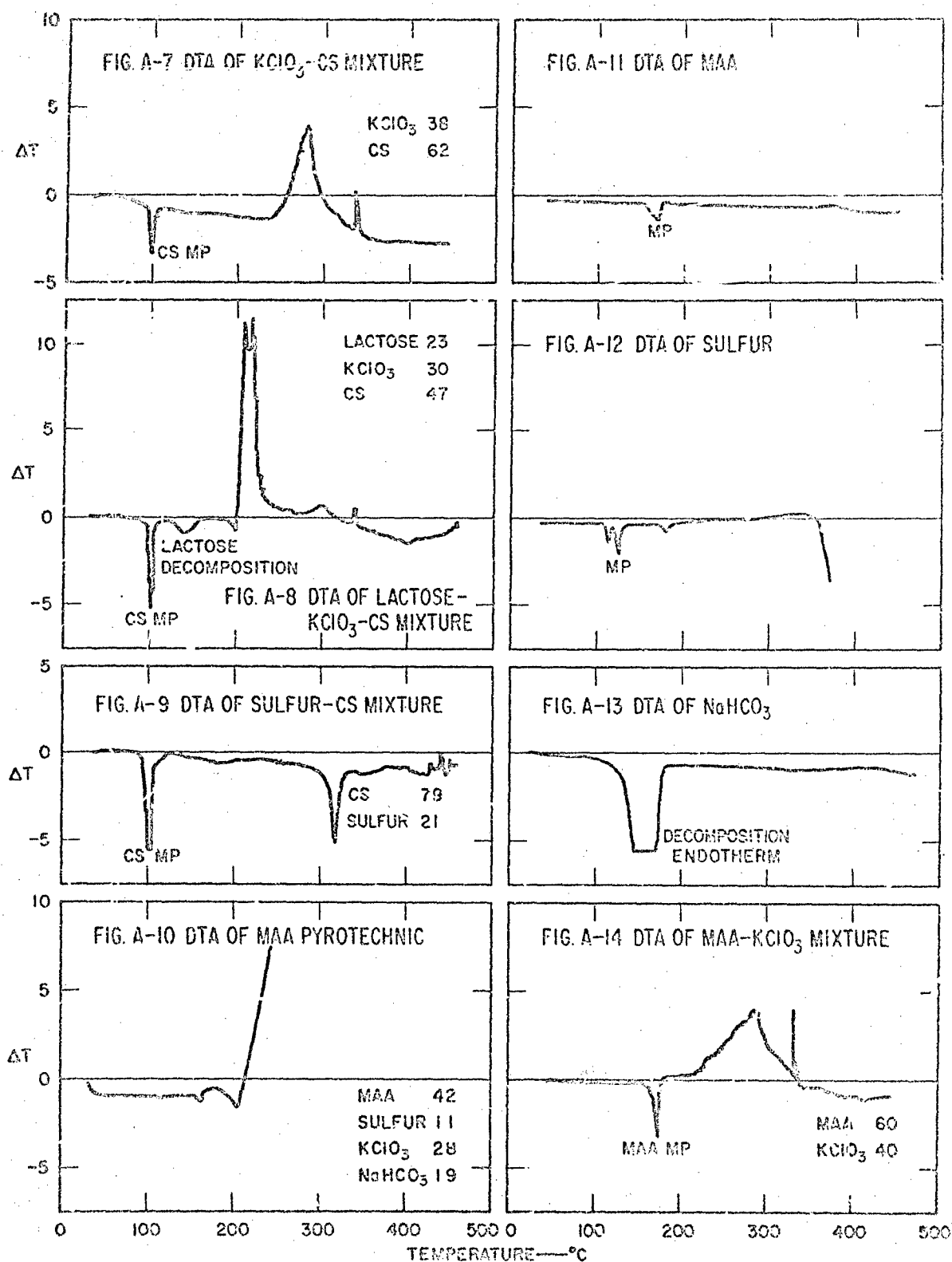
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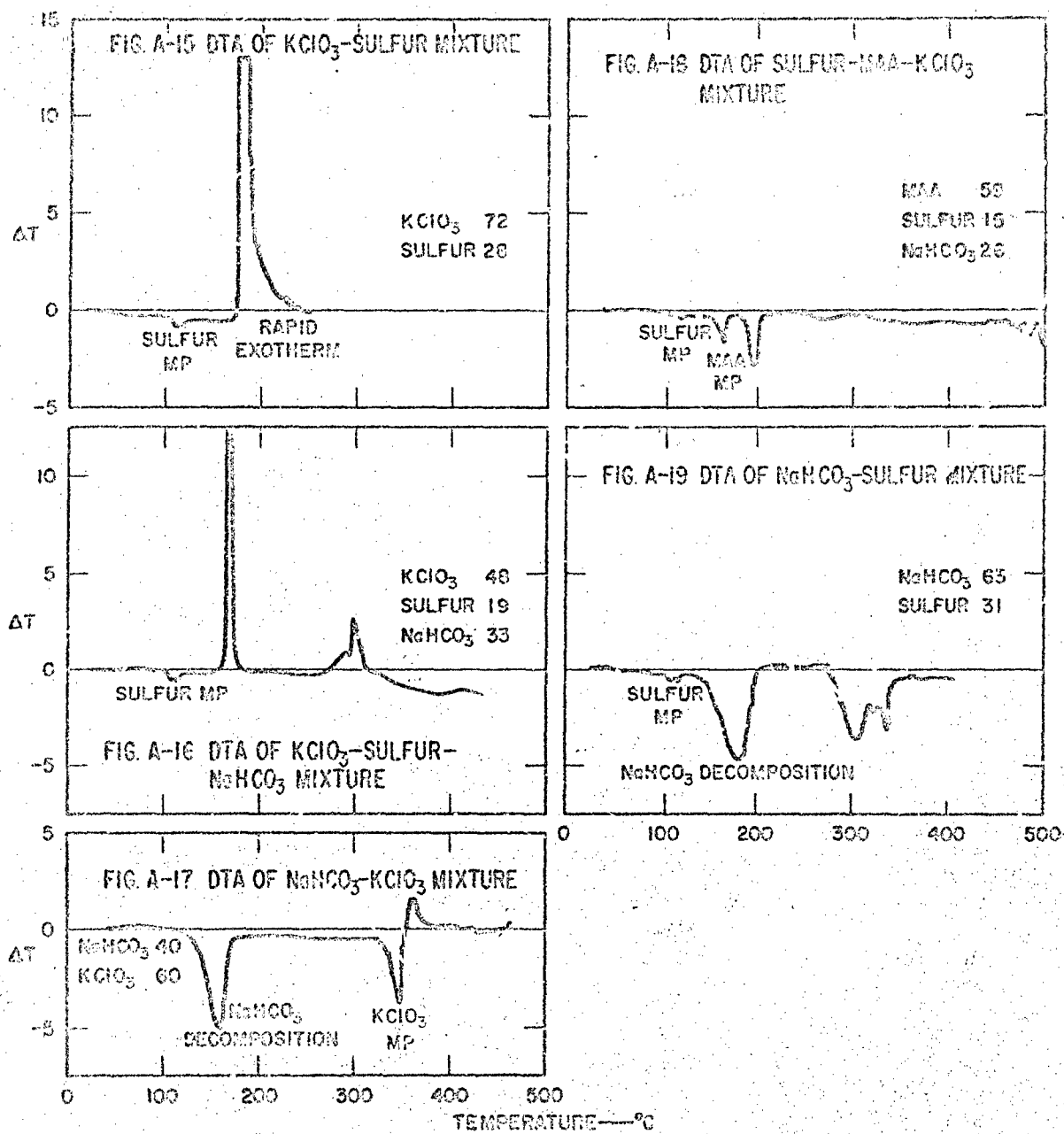
FIG. A-1 THROUGH A-6





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FIG. A-7 THROUGH A-14



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FIG. A-15 THROUGH A-19

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13. ABSTRACT			
<p>(U) This document reviews recent work accomplished toward the development of an understanding of the processes involved in pyrotechnic dissemination. The experiments which were performed to investigate these areas included adiabatic self-heating (ASH) measurements, differential thermal analysis (DTA) measurements, burning rate measurements as a function of pressure, temperature profile measurements in the combustion zone, and agent yield measurements utilizing a total recovery technique.</p> <p>The ASH experiments defined the activation energy of a typical pyrotechnic and of binary mixtures of its ingredients and showed that a burning-rate derived activation energy is necessarily unreliable because of its dependence on the physical process of heat transfer. The DTA measurements defined the endotherms and exotherms to be expected as a function of temperature. Burning rate studies indicated that pyrotechnics have a burning rate law which resembles that of solid rockets. Agent yield measurements demonstrated that larger pyrotechnics were more effective than small ones.</p>			

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 Combustion  
 Agent Yield  
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Gentlemen:

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Would you kindly attach the enclosed overlays to cover the present "Acknowledgments" section on the reverse of the title page.

Very truly yours,

William C. Thuman, Physical Chemist  
Department of Molecular Physics

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Enclosures

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Mr. Lionel A. Dickinson directed these studies from their inception through February 1967, when he accepted the position of Director of Advanced Technology, Naval Ordnance Station, Indian Head, Maryland. Although Mr. Dickinson left the Institute prior to the writing of this report, the authors wish to give him full credit for the concepts and accomplishments described herein.

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